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INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part II. The Issue of Reactivity

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a follow-up review/analysis effort. The follow-up effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

J.G. Calvert, Ohio State University, Columbus, Ohio, and H.E. Jeffries, University of North Carolina, Chapel Hill, N.C., reviewed the papers presented at the 1976 International Conference on Oxidants related to the issue of reactivity, and offered their views on the current status of research in the field, resolutions of the issue, and the need for additional research.

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Part II. The Issue of Reactivity

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a follow-up review/analysis effort. The follow-up effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

J.G. Calvert, Ohio State University, Columbus, Ohio, and H.E. Jeffries, University of North Carolina, Chapel Hill, N.C., reviewed the papers presented at the 1976 International Conference on Oxidants related to the issue of reactivity, and offered their views on the current status of research in the field, resolutions of the issue, and the need for additional research.

CONTENTS

ABSTRACT iii

FIGURES v

TABLES vi

INTRODUCTION 1
B. Dimitriades and A.P. Altshuller

THE ISSUE OF REACTIVITY 3
B. Dimitriades and A.P. Altshuller

REVIEW AND ANALYSIS 5
J.G. Calvert

Introduction 5
Review of the International Conference Papers Related to the Issue of Reactivity 6
General Conclusions Concerning the Issue of Reactivity 29
Comments by H.E. Jeffries 33

REVIEW AND ANALYSIS 35
H.E. Jeffries

Introduction 35
Discussion 38
Recommendations for Future Research 70
Comments by J.G. Calvert 70

REFERENCES 71

FIGURES

REVIEW AND ANALYSIS - H.E. Jeffries

Number		Page
1	"Ultra Clean" air irradiation in cylindrical 400-liter glass/teflon EPA chamber.	47

TABLES

REVIEW AND ANALYSIS - J.G. Calvert

Number		Page
1	Photolytic Rate Constants Estimated from the Formulations of Chang and Weinstock . . .	9
2	Comparison of Relative Photolytic Rate Constants Employed by Chang and Weinstock and Other Workers	10
3	Estimated HO from EPA Chamber Studies of Organic Reactivities	25

REVIEW AND ANALYSIS - H.E. Jeffries

Number		Page
1	Comparison of Smog Chamber and Computer Simulation Studies.	43
2	Computer Simulation Results for the September 8, 1976 RTI Outdoor Smog Chamber Propane and NO_x Experiment.	57
3	Computer Simulation Results at Initial Conditions near Rural Conditions.	58
4	Comparisons of Inorganic Portions of Chang and Weinstock Mechanisms with Dodge Mechanism for Propane	59
5	Comparison of Organic Portion of Chang and Weinstock Mechanism with Dodge Mechanism for Propane	60

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INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted out by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of natural organic emissions. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow, along with the experts' comments on each other's reports.

THE ISSUE OF REACTIVITY

Basil Dimitriades and A. Paul Altshuller

In regard to reactivity, the questions most urgent and directly related to the oxidant control problem pertain (a) to the effectiveness of "substitution" (of less reactive for more reactive organic emissions) as an approach to oxidant control and (b) to the identification of those organics that are essentially of no concern insofar as the oxidant problem is concerned. The more specific questions that need to be answered follow.

- Does the scientific evidence alone justify formulation and enforcement of *interim* substitution rules more stringent than Rule 66?
- Considering all relevant factors, e.g., impact upon urban air quality, impact upon rural air quality, cost, technological feasibility, etc., would it be preferable to abandon altogether the idea of developing interim improved substitution rules and devote instead and immediately all attention and resources to development of methods and practices for "nearly indiscriminate" control of organics?
- Are there any organics so little reactive that they would neither cause nor contribute significantly to oxidant buildup at problem levels under any circumstances?

There are also the relatively less important questions regarding definition of reactivity and validity of the data and procedure used to classify organics based on their relative abilities to contribute to the urban oxidant problem.

Of these questions, the one on the merits of substitution has been discussed both internally in EPA and informally at an open meeting (EPA's Forum on Solvent Substitution, Chicago, Ill., Oct 13-14, 1976); there was a consen-

sus that substitution will have a small but possibly significant benefit upon urban air quality — more precisely, the air quality in the vicinity of the source area — but will have less or no benefit upon distant downwind areas. Although not quantitatively answered, the question was nevertheless treated adequately so that further discussion here is not warranted. Also, the question on merits of "nearly indiscriminate" control is outside the scope of this review, since it calls for judgments on cost, technological feasibility, etc.

The question that is offered as the specific subject of this review is the one regarding the possible existence and identities of organics incapable of causing oxidant problems. This question was discussed at the International Conference and drew conflicting answers. The specific issue here is centered around the method used for reactivity-rating the various organics and for defining the borderline separating the reactive ones from those of *virtually no concern with respect to the oxidant problem*. In general, two distinctly different approaches were proposed: The smog chamber approach applicable to all organics (4), and the mathematical modeling approach (5) applicable, at present, to certain organics only, namely, paraffinic and olefinic hydrocarbons and aliphatic aldehydes. To facilitate the process of judging these two and/or any other approaches, it would perhaps be useful to break the issue down to two parts: One pertaining to the reactivity-rating of the organics, especially of those of low reactivity, and one pertaining to the positioning of the borderline separating the almost totally unreactive ones from the reactives. Judgments that must be made are on:

- whether the two proposed approaches agree or disagree in results and to what extent,
- whether one or the other or the two approaches combined in some way or any other approach yields the most reliable results, and
- the specific additional research needed to substantiate or refute these first judgments.

REVIEW AND ANALYSIS

J. G. Calvert

INTRODUCTION

In this report a critical examination will be made of the specific papers related to reactivity presented at the International Conference on Photochemical Oxidant Pollution and Its Control (Raleigh, N.C., September 12-17, 1976). Furthermore, reference to other pertinent scientific information will be made in an attempt to examine the results and conclusions related to oxidant control strategy and the reactivity issue. As charged by the Officers of the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency (1), an effort has been made to (a) examine the reported evidence and viewpoints for conflicts; (b) make judgments on strengths and weaknesses of opposing viewpoints or evidence, and based on such judgments, attempt to reconcile conflicting viewpoints and evidence; and (c) derive a factual or judgmental conclusion regarding resolution of the status of the issue, and offer recommendations for additional research.

This report has been organized to present first a critical review of each of the conference scientific papers related to the reactivity issue. In the second part of this report an attempt is made to face those questions that the EPA has pinpointed as the most urgent and directly related to the oxidant control problem. A major question of interest to the agency is the possible existence and identities of organics incapable of causing oxidant problems. We are concerned with the reactivity rating of the organics, especially those of low reactivity, and the positioning of the borderline separating the "almost totally unreactive" ones from the reactives.

In our considerations of these issues we must compare the conclusions based upon smog chamber experiments and those based upon chemical modeling of the atmospheric changes. Finally we must answer the questions: (a) To what extent do the two approaches (chamber versus modeling) agree or disagree? (b) Does one or the other of the two approaches combined in some way yield the most reliable results? (c) What additional research is needed to substantiate or refute these first judgments?

A REVIEW OF THE INTERNATIONAL OXIDANT CONFERENCE PAPERS RELATED TO THE ISSUE OF REACTIVITY

"Net Ozone Formation in Rural Atmospheres" by Tai Yup Chang and Bernard Weinstock.

Chang and Weinstock have developed a simple chemical reaction scheme to rationalize the results observed in the EPA and General Motors Corporation smog chamber experiments utilizing "unreactive" hydrocarbons, C_2H_2, C_3H_8, and $n\text{-}C_4H_{10}$. An effort is made to introduce into the homogeneous mechanism, certain heterogeneous steps peculiar to the smog chamber. After identifying such smog chamber peculiarities, those not expected to occur in the atmosphere were removed from the mechanism, and simulations were made of the chemistry of the "unreactive" hydrocarbons in a rural atmosphere. The authors conclude from their study that "unreactive" hydrocarbons released in the urban atmospheres contribute little either to the generation of elevated rural ozone levels or to the increase of elevated levels already present. They conclude that the major cause of elevated rural O_3 levels is the transport of high O_3 concentrations generated in urban areas and additional O_3 produced by reactions of fresh reactive hydrocarbon (RH) and NO_x emissions from local rural sources, both natural and man-made. The authors' analysis is at variance with the new EPA Policy Statement that severe control of all hydrocarbons, without regard to reactivity, will be necessary to reduce elevated rural O_3 levels.

There are some major questions that should be considered here relating to the chemical modeling of Chang and Weinstock. First the formulation of the model as given appears to provide an artificial source of organic radicals of

unlimited supply. Note in the following sequence that the RO_2 radicals formed by HO-radical attack on HC_2 (Reaction 35), react in Reaction 46 to create a fraction β of the time, an aldehyde (RCHO), which has gained a carbon atom:

$$HC_2 + HO \rightarrow RO_2 + H_2O \quad (35)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (42)$$

$$RO + O_2 \rightarrow \beta RCHO + (1 - \beta)CH_2O + HO_2 \quad (46)$$

$$RCHO + HO \rightarrow RCO_3 + H_2O \quad (38)$$

$$RCHO + h\nu \rightarrow RO_2 + HO_2 + CO \quad (9)$$

$$RCO_3 + RCO_3 \rightarrow 2RO_2 + O_2 \quad (54)$$

$$RCO_3 + NO \rightarrow RO_2 + NO_2 \quad (43)$$

The RCHO species in turn provides a reactive oxidizing agent for NO through the radicals RCO_3, RO_2, and HO_2. The RCO_3 radical may reform RO_2 in Reactions 42 and 43, and may in principle provide an unlimited new supply of these radicals that is never depleted. It seems to me that the use of less general reactions that do not allow an unrealistic source of RO_2 would be more suitable and very few additional reactions need be employed. Thus the degradation of C_3H_8 by the way of real chemical entities is important to maintain the mass balance: $C_3H_8 \rightarrow$ iso-$C_3H_7O_2 \rightarrow$ iso-$C_3H_7O \rightarrow CH_3COCH_3$ and $CH_3 + CH_3CHO$; $C_3H_8 \rightarrow$ n-$C_3H_7O_2$; n-$C_3H_7O \rightarrow C_2H_5CHO + CH_2O + C_2H_5O_2$; $CH_3O_2 \rightarrow CH_3O \rightarrow CH_2O \rightarrow HCO_3 \rightarrow HCO_2 \rightarrow CO_2$, CO; $C_2H_5O_2 \rightarrow C_2H_5O \rightarrow CH_3CHO + CH_3 + CH_2O$, etc.

The rates of all of the reactions that are initiated by sunlight absorption employed by Chang and Weinstock appear to be unusual. Specifically the equation given for k_1 ($NO_2 + h\nu \rightarrow NO + O$) must be reported here incorrectly. If the authors really used this to determine the values of k_1, and in turn used these estimates of k_1 to establish the other photochemical rates as they outline in their table on pages 13 and 14 of their Appendix, then practically no chemical change would occur or would be expected to occur in their simula-

tions. See Table 1 of this review. The values estimated from the Chang and Weinstock Equation 1 may be compared with those estimated in previous studies. At the maximum solar intensity Chang and Weinstock's value for k_1 = 0.0149 min^{-1}, compared to the value of 0.46 min^{-1} estimated by Calvert for Los Angeles on November 5, 1973 (4). Thus the Equation 1 presented by Chang and Weinstock gives values about a factor of 31 too low. As stated previously, this must be an error introduced in the typing or preparation of the manuscript and probably does not reflect actual values used in the simulations. If they are the values employed, then the results of the simulations are meaningless. This point must be cleared up, of course, if the conclusions of Chang and Weinstock are to be accepted.

Whatever the value of k_1 chosen by Chang and Weinstock, the other photochemical rate constants for HONO, CH_2O, RONO, etc, are derived from this k_1 value for the given time. In Table 1 reference to a few of the other values should be made to illustrate the magnitude of the photochemical rates employed. The estimated k_2 (HONO + $h\nu \rightarrow$ HO + NO) from Chang and Weinstock's work reaches a maximum of 1.0×10^{-3} min^{-1}; this is a factor of 100 less than that estimated in our previous studies (5). The most recent work of Derwent and Cox (6) requires that the estimate of Johnston and Graham (7) of the extinction coefficients of HONO be increased significantly. We find that the use of the new data together with a reasonable solar distribution function leads to a value as high as 0.20 min^{-1} for k_2. Also the extinction data for CH_3ONO do not support the value picked for k_{10} (RONO + $h\nu \rightarrow$ RO + NO); it is 70-times smaller than the value I would choose. As I stated previously, the k_1 values calculated from the Chang and Weinstock Equation 1 may not be those actually employed because of some mechanical error.

If some error in the manuscript for the k_1 equation exists, then the relative values of these photolytic processes should give us some feel for the presumed importance of each step. In Table 2 shown here, I have compared the relative values for these constants chosen by Chang and Weinstock and others, taking the k_1 for NO_2 photolysis = 1.0. The only two very unusual rates chosen on this basis are those for HONO and RONO. We have discussed the need for a much larger value for the HONO photolysis rate constant previously. Our

TABLE 1. PHOTOLYTIC RATE CONSTANTS ESTIMATED FROM THE FORMULATIONS OF CHANG AND WEINSTOCK

Hour	k_1, min^{-1} Chang and Weinstock	k_1, min^{-1} Calvert (3)	Apparent First Order Rate Constants, min^{-1} k_2 (HONO)	k_3 (k_4,k_5,k_6 k_{10})	k_7 (CH_2O,a)	k_8 (CH_2O,b)	k_9(RCHO)
0700	2.8×10^{-7}	5×10^{-2}	1.9×10^{-8}	9.8×10^{-10}	1.3×10^{-9}	3.1×10^{-9}	3.4×10^{-10}
0800	3.3×10^{-4}	1.9×10^{-1}	2.2×10^{-5}	1.2×10^{-6}	1.6×10^{-6}	3.6×10^{-6}	4.0×10^{-7}
0900	3.1×10^{-3}	3.2×10^{-1}	2.1×10^{-4}	1.1×10^{-5}	1.5×10^{-5}	3.4×10^{-5}	3.7×10^{-6}
1000	8.2×10^{-3}	4.0×10^{-1}	5.6×10^{-4}	2.9×10^{-5}	3.9×10^{-5}	9.0×10^{-5}	9.8×10^{-6}
1100	1.3×10^{-2}	4.4×10^{-1}	8.8×10^{-4}	4.5×10^{-5}	6.1×10^{-5}	1.4×10^{-4}	1.5×10^{-5}
1200	1.5×10^{-2}	4.6×10^{-1}	1.0×10^{-3}	5.2×10^{-5}	7.0×10^{-5}	1.6×10^{-4}	1.8×10^{-5}
1300	1.3×10^{-2}	4.4×10^{-1}	8.8×10^{-4}	4.5×10^{-5}	6.1×10^{-5}	1.4×10^{-4}	1.5×10^{-5}
1400	8.2×10^{-3}	4.0×10^{-1}	5.6×10^{-4}	2.9×10^{-5}	3.9×10^{-5}	9.0×10^{-5}	9.8×10^{-6}
1500	3.1×10^{-3}	3.2×10^{-1}	2.1×10^{-4}	1.1×10^{-5}	1.5×10^{-5}	3.4×10^{-5}	3.7×10^{-6}
1600	3.3×10^{-4}	1.9×10^{-1}	2.2×10^{-5}	1.2×10^{-6}	1.6×10^{-6}	3.6×10^{-6}	4.0×10^{-7}
1700	2.8×10^{-7}	5×10^{-2}	1.9×10^{-8}	9.8×10^{-10}	1.3×10^{-9}	3.1×10^{-9}	3.4×10^{-10}

estimates suggest that a value about 3.7-times larger than that chosen would be more appropriate. In the case of RONO I feel that a value about 71-times larger should be used.

TABLE 2. COMPARISON OF RELATIVE PHOTOLYTIC RATE CONSTANTS EMPLOYED BY CHANG AND WEINSTOCK AND OTHER WORKERS

Compound	Chang-Weinstock	Demerjian, Kerr, Calvert (4)	S.A.I.(7)
NO_2	1.0	1.0	1.0
HONO	0.068	0.25	0.21
H_2O_2	0.0035	0.0063	0.0031
RO_2H	0.0035	-----	-----
RCO_3H	0.0035	-----	-----
$O_3(^1D)$	0.0035	0.0071	0.0133
CH_2O(a)	0.0047	0.0042	0.0025
CH_2O(b)	0.011	0.011	0.0081
RCHO	0.0012	0.0052-0.0009	0.0016
RONO	0.0035	0.25	-----

HONO and RONO are termination products that stop the oxidation chains unless they photolyze to regenerate the HO and RO radicals. A choice of values for the photolysis constants for these compounds that is too small leads to an underestimation of the rates of chemical change in the simulation. The effect of a more realistic choice for these constants should be investigated.

In one phase of the Chang and Weinstock work they have utilized the modeling approach of Pitts et al. (8), who have assumed a constant HO-source in their smog chamber as a possible technique to employ for atmospheric simulations. This approach is not one I favor. If the chain sequence is initiated by an unknown reactant forming HO-radicals, then detailed simulations lose their meaning, and the utility for extrapolation to the real atmosphere is lost. All such an approach does is to hide our ignorance and avoid identification of the important chain initiating steps. There is not reason to

believe this source to be of infinite capacity to supply radicals at a constant rate throughout the run.

The choice of $NO + NO_2 + H_2O \rightleftharpoons 2HONO$ rate constants by Chang and Weinstock are those found by Wayne and Yost (9) for a capillary tube reactor; we also employed these numbers in treating data from a number of early chamber data (5). These numbers seem to be unusually high for use in a large chamber today. The alternative use of k_{20} $(NO + NO_2 + H_2O \rightarrow 2HONO) = 1.0 \times 10^{-11}$ $ppm^{-2}min^{-1}$ for the atmospheric simulations is also unusual in my opinion; the number is 50-times smaller than that observed recently in a chamber study by Chan et al. (10); in this work a significant effort was made to minimize the heterogeneous reaction pathways for these reactions (very low surface/volume ratio employed), but the authors recognized that these estimates were at best upper limits to the true homogeneous rate constants. The, as yet unpublished, work of Kaiser and Wu from which Chang and Weinstock pick their number, should be compared with that of Chan et al., and reasons for the choice given. In any case, for most atmospheric conditions involving the dilute NO_x mixtures, the formation of HONO through Reaction 20 should be slow.

On page 6 of the Chang and Weinstock paper, the point is made that rural NO_x values are probably below the 5-10 ppb reported in the 1974 Midwest Study (19). When one considers the relatively large impact of NO_x from auto traffic, power plants, homes, chemical plants, and other stationary sources located near the "rural" area, then levels of NO_x as high as 10 ppb are not unexpected in my view.

It is important to learn more detail about the method used by Chang and Weinstock to keep the NO_x constant in their simulations shown in their Table 2. Was new NO_2 (not NO) added as $HONO_2$, $RONO_2$, etc, depleted the NO_x? If NO was added to keep NO_x constant in these simulations then it is hardly a fair test for O_3 buildup, since the ozone will be titrated in part by the rapid reaction, $NO + O_3 \rightarrow NO_2 + O_2$. This point should be clarified by the authors.

In spite of the several questions that appear to require some clarification before the results can be considered definitive, it is interesting to see

in the data of Table 3 of Chang and Weinstock that the mechanism outlined by them does predict that the presence of only 0.1 ppm of C_3H_8 in air of a typical 0.04 ppm background O_3 level, increases the $[O_3]$ to 0.074 ppm on the first day of the irradiation. Also during the first day slight increases (0.10 to 0.114 and 0.15 to 0.153) in $[O_3]$ occur with 0.1 ppm C_3H_8 insertion into an air mass with higher preexisting $[O_3]$. With alternative choices in the mechanism as outlined above, it would be interesting to see what changes, if any, would be found.

The authors contend that the hydrocarbon analyses made in the 1974 Midwest Study show no evidence of accumulation of less reactive species that would be characteristic of an aged air mass that has had no significant new impurity input. The presence of alkenes in the analysis certainly suggests that new RH impurity has been added. However the levels of acetaldehyde reported suggest that some significant chemistry involving RH oxidation has occurred in these air masses as well.

The potential role of C_3H_8 or other "unreactive" RH compounds in photochemical smog development in urban air masses remains unresolved in my mind. It is unlikely that any old air mass will contain only "unreactive" hydrocarbons; it is most reasonable that certain oxidation products (CH_2O, CH_3CHO, etc.) should build up to significant levels. Although these compounds are reactive both photochemically and toward HO-radicals, they will continue to form in an aged air mass as the RH oxidations proceed. A significant level of these species should persist for several days. Chang and Weinstock do not consider this issue and start their simulations with only C_3H_8 (0.10 ppm), CO (0.20 ppm), CH_4 (2 ppm), and NO_2 (10 ppb). Photolytic generation of radicals in their system initially is restricted to those derived from O_3 photolysis largely:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow 2HO$$

This rate is very low. In my opinion a more realistic model would assume an initial $[CH_2O]$ and $[CH_3CHO]$ carryover as products of the RH oxidation reac-

tions that lead to the C_3H_8-rich air mass they choose. Even 0.01 ppm of each of these aldehydes would provide a more significant rate of radical generation than the O_3 photolysis. Thus an artificially low rate of chemical change may be present in the Chang and Weinstock simulations.

The acceptance of the Chang and Weinstock conclusion that "unreactive" hydrocarbons will not enhance rural ozone formation may be correct, but this has not been proven by the study. Acceptance of this or some other conclusion should await the resolution of the several problem areas that seem to exist in this work.

"Multiday Irradiation of NO_x-Organic Mixtures" by W. A. Glasson and P. H. Wendschuh.

Glasson and Wendschuh have simulated experimentally the photochemical smog formation in single day and multiday irradiations of different polluted air masses. The experiments were carried out in the General Motors Corporation smog chamber. Irradiations of a typical urban hydrocarbon mixture and several automotive paint solvents of different "reactivity" were made in dilute mixtures with NO_x in air. In the case of the most reactive of the three paint solvents, the $[O_3]$ peaked much higher than with the other solvents (0.45 ppm) at 6 hours irradiation, but after 24 hours all solvent mixtures had similar $[O_3]$ levels (0.15 ppm). In transport simulations (light and dark periods) with a variety of reactive and unreactive hydrocarbons, the ozone maximum during the "second day" irradiation remained higher for the more reactive RHs; on the "third day" the highest maximum $[O_3]$s, 0.12 and 0.13 ppm, also came from the reactive species cis-2-butene and auto exhaust, respectively.

In another series of runs the initial $[NO_x]$ was varied while the initial concentration of the typical urban hydrocarbon mixture was held constant at 0.935 ppm C. Typical NO_x-inhibition curves for $[O_3]$ were found. However the $[NO_x]$ required for maximum $[O_3]$ increased with each succeeding day. The authors conclude from these results that reductions in urban $[NO_x]$ will increase $[O_3]$ on the first day (urban air mass), slightly reduce O_3 on the second day (rural), and have little effect on O_3 on the third day (rural).

Thus they feel that the result of reducing urban NO_x concentrations may be to trade-off higher $[O_3]$ exposures in the urban population centers for small effects in the sparsely populated rural environment.

One important feature of the Glasson and Wendschuh study is the determination of the concentration dependence of the CH_2O product on time. It is important to recognize that the CH_2O that formed and survived photochemical decomposition and HO-radical attack in the multiday irradiation is an appreciable fraction of the orginial RH used. See Table IV of the more complete paper (GMR-2236) (11). From these data we may estimate (taking into account the dilution rate of 0.0015% sec^{-1}) that about 1 ppm of CH_2 is formed for each ppm of hydrocarbon reacted. Without a knowledge of the complete product distribution as a function of time, it is not possible to accurately assess the RH to CH_2O conversion efficiency here, but it is clear that a large amount of CH_2O (and presumably other aldehydes) are formed during these oxidations. These compounds provide an excellent radical source, and even the unreactive RH species are stimulated to oxidize and provide for O_3 formation, provided that sufficient NO_x is present to supplement the RH-RCHO mixture. This consideration is particularly important in formulating models to simulate long-range transport transport of urban air masses.

In the multiday irradiations of the NO_x-organic solvent mixtures the ozone levels eventually approached the same value; this suggests to me that there is some reasonable reactivity of the ultimate "unreactive" mixture of the A and B solvents as well as the "reactive" C solvent. The formation of the light-absorbing aldehydes in all mixtures may ultimately control the reactivity of the final "unreactive" mixtures that result in the later days of the irradiation.

One might question whether the square wave pulse of "sunlight" employed in the General Motors Corporation experiments provides a realistic simulation of the true solar day irradiations. The somewhat low value of the $k_1 (NO_2 + h\nu \rightarrow NO + O) = 0.25\ min^{-1}$ used in the chamber should give a depressed O_3 compared to the real atmosphere. It is not clear from the present data given that this value of 0.25 min^{-1} represents the actual best value of k_1 in these recent

chamber experiments. Simulations of chamber experiments suggest that at any given time t during chamber irradiations of dilute NO_x mixtures as employed here, the product ratio $[NO]_t[O_3]_t(23)/[NO_2]_t \simeq k_1(min^{-1})$. The data for 2.1 and 2.6 min (times when NO, NO_2, and O_3 are all measurable), taken from Figure 2 of the Glasson and Wendschuh paper, give $k_1 \simeq 0.13\ min^{-1}$. In any case the somewhat low k_1 value will alter the $[O_3]$-time profile from that which would be observed in the real atmosphere. It is not clear that this effect would alter the results and conclusions significantly, but the difference remains as an uncertainty.

Another factor that may lead to chamber results that are somewhat unique compared to those expected in the true atmosphere is the wavelength distribution of the lamps in the chamber. The transmission of the Pyrex glass tubes in which the lamps were housed may restrict from the chamber the 3000-3100 Å region unduely, and hence the true impact on the CH_2O product and the induced rate of oxidation of the RH mixtures may not be representative of those expected in the atmosphere. However the comparison of the expected chamber distribution to the solar distribution suggests that this problem may not be important here (12). However actual measurements in the chamber should be made to test this properly.

"Smog Chamber Simulation of Los Angeles Pollutant Transport" by William A. Glasson.

This paper presents the results of the 24-hour irradiation (equivalent to 12-hour solar day) of typical urban Los Angeles RH-HO_x impurity mixtures that are intended to simulate pollutant transport during the day from Los Angeles to Riverside and San Bernadino. The effects of variations of $[NO_x]$ emissions on the generation of O_3 within the air masses were studied. The author concluded that the downwind oxidant levels are only slightly affected by large changes in NO_x emissions, while reduced NO_x emissions in the Los Angeles area will lead to an increased oxidant level in downtown Los Angeles.

The problems of chamber intensities below those of solar intensities, discussed in the preceding section of this review, remain as does the possible

problem of differences in wavelength distributions of the chamber and the sunlight. It is apparent from $[O_3]$ versus time data given in Figure 3 of this paper that a significant delay in O_3 formation is seen at higher $[NO_x]°$. Thus at 0.85 ppm = $[NO_x]°$, 7 hours of irradiation are necessary to reach the national air quality standard (1 hour maximum) of 0.08 ppm. While at 0.099 ppm NO_x, this standard is exceeded in somewhat over 1 hour of irradiation. However also note that 0.77 ppm of NO_x leads to about twice the $[O_3]$ after 24 hours (0.165 ppm) that 0.099 ppm = $[NO_x]°$ gives at this time (0.085 ppm). Thus it appears to me that the effect of ozone levels in transported air masses can be significantly elevated downwind when larger NO_x levels are employed. The effect of this delay on population exposure to ozone is not clear however. Perhaps a more realistic criterion for ozone control strategy should be designed in the future in terms of minimization of the population exposure. Thus assume the city is divided into n different blocks of equal area, and N_i is the population in the ith area. Then perhaps we should attempt to minimize the total O_3 dosage of the total population over each 24-hour period:

$$\sum_{i=1}^{n} \int_{0}^{24\ hr} [O_3]_t^i \, [N_i]_t \, dt = \text{Ozone-Population Dosage}$$

When the density of the population over which the air mass is transported is fairly uniform, then the $\int [O_3]dt$ function is a proper measure of the function to be minimized. The integral ozone is not altered much over the range of [NO] employed by Glasson. If the density of population is weighted toward downtown LA, where the Riverside air mass may originate in the early morning hours, then the total function above will favor the use of higher $[NO_x]$ values on the basis of O_3 exposure alone.

However, control stategy should take a more educated view of the exposure of the population to the many insults from impurities present in the atmosphere, and focus of O_3 exposure alone should not be made. One should in principle minimize the total impurity insult to the population to optimize the control strategy:

$$\text{Total 24-hr insult} = \sum_{i=1}^{n} \int_{0}^{24\ hr} a[O_3]_t^i \, [N_i] \, dt + \sum_{i=1}^{n} \int_{0}^{24 hr} b[NO_2]_t^i \, [N_i] \, dt \; . \; .$$

The quantities a, b, etc., are proportional to the relative intensities of the health effects induced by each impurity at the same concentration. The complete function for the 24-hour insult would include terms for PAN, $HONO_2$, CH_2O, HONO, $RONO_2$, etc. The best choice of NO_x in their early morning hours will depend upon the magnitude of the NO_2, PAN, $HONO_2$, CH_2O, HONO, and other terms as well as that of the O_3 term. If the penalty paid for the high NO_x levels in the early morning, as determined by the sum of all of the terms other than that of O_3, is greater than the benefit achieved by the lower O_3 term, then obviously the strategy of high NO_x is not sound. Control strategies of sufficient sophistication to attempt such analyses as outlined above should be considered in planning if reasonable trade-offs in pollutant emissions are to be attempted. Obviously it is not enough to consider only the effect of lowered $[O_3]$ at early times through increased $[NO_x]$ in the morning hours.

It would be instructive to have multiday exposure experiments as shown in Figure 4 for NO_x-RH experiments with new insertions of impurities, since this would represent much better the multiday exposure case than allowing the drift of an air mass that is unaltered by insertions. If such a case does not occur, it is relatively unimportant in health effects considerations, since no human activity exists in the area if no emissions are added.

"Hydrocarbon Reactivity and the Role of Hydrocarbons, Oxides of Nitrogen, and Aged Smog in the Production of Photochemical Oxidants" by James N. Pitts, Jr., Arthur M. Winer, Karen R. Darnall, Alan C. Lloyd, and George J. Doyle.

The study presents a reactivity classification for a variety of atmospheric impurities (alkanes, alkenes, aromatics, oxygenates, natural hydrocarbons, etc.) based upon the rates of the reactions with the HO-radical. The work is built upon the premise that the HO-radical is the dominant chain carrier in photochemical smog; it is also implicitly assumed that the HO-reactions are rate determining steps in the subsequent oxidation of NO to NO_2 and O_3 production. The reactivity of the organics is divided into a five-class reactivity scale in which each class spans a factor of 10 in magnitude of the reaction rate constant. The authors suggest that a comparison of HO-

rate constants for different compounds will provide a good insight into the O_3 forming potential for this species in the atmosphere.

This study on the evaluation of the influence of various RHs on smog formation is an important guide to determine the relative removal rates of RHs in the atmosphere. However, if our major concern in the development of control strategy remains focused upon the maximum ozone level that is reached in an air mass, then the relative rates of HO-attack on hydrocarbons are only one part of the necessary input for prediction. The O_3 level during daylight hours is controlled by the existing $[NO_2]/[NO]$ ratio and the values of k_1 ($NO_2 + h\nu \rightarrow NO + O$) for the particular solar intensity present, when, as is often the case in urban air masses, the rate of O_3 reaction with NO ($NO + O_3 \rightarrow NO_2 + O_2$) is the dominant O_3 loss pathway. Thus, for these conditions at a given NO_x level, the important fundamental factors controlling ozone are the concentrations of HO_2 and RO_2 radicals that increase the $[NO_2]/[NO]$ ratio and hence control the $[O_3]$:

$$HO_2 + NO \rightarrow HO + NO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

These RO_2 and HO_2 concentrations at any instant are in turn directly related to the [HO] levels since each radical is formed following HO-radical attack on RHs:

$$HO + RH \rightarrow H_2O + R$$

$$R + O_2 \rightarrow RO_2$$

$$HO + CO \rightarrow H + CO_2$$

$$H + O_2 + M \rightarrow HO_2 + M$$

Note that the HO-radical level is established by the balance between the rates of the primary reactions that form it and those that destroy it. To consider the potential of a mixture for O_3 formation in the atmosphere then requires a knowledge of the primary HO-formation rates. Demerjian, Kerr, and Calvert

(5), and Calvert and McQuigg (13) have concluded that the aldehydes will probably be the dominant primary source of HO_2 radicals for high smog conditions, while the reaction $HO_2 + NO \rightarrow HO + NO_2$ is the likely dominant source of HO-radicals for these conditions. Thus it can be seen that if predictions concerning the ozone-forming potential of a mixture are to be made realistically, not only the HO-radical rates with RH are important, but equally important are the primary routes that form the radicals and the rates of their generation. What may be a very reactive alkane will not produce ozone unless the $NO-NO_2$ levels are sufficiently high and some primary source of HO_2 and/or HO radicals is present to generate these radicals at a significant rate.

The observations of Pitts et al. that propane and n-butane can react to produce substantial amounts of ozone, based upon smog chamber results, confirms the observations of many others who have done smog chamber experiments. However this result should be considered in some detail. The reactivity of RHs of low reactivity in smog chambers is in part a consequence of seemingly unique radical sources (HONO, CH_2O,...) present in the chamber. Unless the RHs are in a suitable reactive mixture of alkenes, aromatics, aldehydes, etc., the induction period for their reaction will likely be much more extensive than that seen in the chambers. However in the real atmosphere it is unlikely that any such radical source will be entirely missing. O_3, CH_2, CH_3CHO, etc., are expected to be present in the old air masses. Thus the RHs of low reactivity can participate in smog formation. Note the estimates made by Calvert for Los Angeles and a typical RH distribution (4). The rate of HO-attack on alkanes amounted to 32.5%; alkenes, 35.1%; aromatics, 20.2%; CO, 12.1% for a typical early morning mixture.

The use of $[HO] = 10^7$ molecules cc^{-1} by Pitts et al. in estimating lifetimes of the different RHs is questionable. Probably this is much too high an estimate for [HO] in rural ambient air. With this concentration of HO the halflife of NO_2 is only 1.5 hours. This seems much too short to fit the existing data. The direct estimate of Wang et al. (14), $[HO] \simeq 5 \times 10^7$ appears to be much higher than that observed by Perner et al., $[HO] \simeq (4\text{-}7) \times 10^6$ molecules cc^{-1} (15). The use of $[HO] = (2.5 \pm 2.0) \times 10^6$ molecules cc^{-1},

which I estimated from the LARPP data for Los Angeles (Nov. 5, 1973) (16), leads to an estimated NO_2 lifetime in the range of 6 hours. So lifetimes shown by Pitts et al., in Table 1 of their paper, may actually be much shorter than the true atmospheric lifetimes in rural environments. A factor of 4 or so greater lifetimes would be my estimate. This does not detract from the utility of the Pitts et al. model as a qualitative indicator of smog forming potential for RHs in a reactive environment. It is the use of these data to predict effects in a rural atmosphere that could be misleading.

The statement of Altshuller and Bufalini quoted in this paper (".. almost every hydrocarbon except methane can produce some oxidant when photooxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen") applied to smog chamber data. It is not clear what will be the case in the real atmoshphere if RH is present with much less abundant radical sources.

The authors state that demonstration by Niki et al. (17), that O_3 and alkenes lead to few radical products, infers that ozone-alkene reactions may not influence the oxidant level. Of course CH_2O, CH_3CHO, CH_2OO, CH_3CHOO and other species are formed in their reactions, and it is highly likely that CH_2OO, CH_3CHOO, and other such species that may be formed will oxidize NO readily:

$$CH_2OO + NO \rightarrow CH_2O + NO_2,$$

and hence increase the O_3 levels. Of course the alehyde formed in these and similar reactions, as well as in the original ozonide cleavage reaction, will be reasonably good radical sources and will influence the oxidant level.

It is pointed out by Pitts et al. that the direct formation of $RONO_2$ by RO_2-NO interaction, $RO_2 + NO \rightarrow RONO_2$, with the C_4-C_6 radicals (R) is an important limitation of HO rate use in predicting oxidant formation. If these reactions are of great significance then the higher alkanes will be poorer oxidant formers. Thus the RO_2s formed by HO-attack on them will not pump NO to NO_2 as HO_2 and the smaller RO_2 radicals do. The net result of an HO attack on a higher hydrocarbon will be the removal of a potential NO_2 and O_3

molecule: $RO_2 + NO \rightarrow RONO_2$. It seems to me if this reaction is important, as these authors suggest, then the pentanes and hexanes should not be as effective as the lighter hydrocarbons in O_3 generation in chamber experiments. This does not seem to be the case however, as illustrated in the smog chamber data summarized by the Western Oil and Gas Association paper (18). Here the C_5 reactions forming O_3 are more efficient than those with C_4, and the C_6 efficiency is about the same as the C_5. The point that Pitts et al. make is an important one, and further work should be done to clarify this apparent problem.

The use of HO rate constant data as one criterion for smog generating ability is a meaningful approach. To use these data to suggest anything quantitative about the ozone levels expected in rural areas is a meaningless exercise unless it is coupled with rates of radical generation and other mechanistic features which control ozone formation.

"Photochemical Reactivity Classification of Hydrocarbons and Organic Compounds" by F.F. Farley (the Western Oil and Gas Association).

A review has been made of available smog chamber data related to hydrocarbon reactivity as measured by $[O_3]$ maxima, and a photochemical reactivity classification of hydrocarbons and organic compounds has been developed. The authors suggest that the wide range of reactivities observed argues for a multiclass reactivity scale.

There are several important points that must be remembered in attempting to evaluate oxidant-forming potential in the atmosphere. Not only smog chamber data should be considered but also the concentrations of the various RH species and the nature of the other components occurring with the given compound. Obviously the rate of reaction of a given hydrocarbon, RH, with the HO-radical ($RH + HO \rightarrow R + H_2O$) is given by:

$$-d[RH]/dt = [RH]\ [HO]k$$

Three factors, the HO-radical concentration, the specific RH concen-

tration, and the rate constant K for the given reaction are involved. The detailed nature of the sunlight-irradiated mixture, that is, the effective rate of generation and destruction of the HO-radical, will establish the [HO]. The relatively unreactive RH may become a major reactant in a given HO-containing environment if its concentration is sufficiently high. Thus it is instructive to note that the estimated rate of reaction of the HO-radical with the most unreactive of the hydrocarbons, methane, in the Los Angeles atmosphere on Nov. 5, 1973, was somewhat greater than that for C_2H_6, C_2H_2, cyclopentane, 2,2,3-, 2,3,3-, and 2,2,4-trimethylpentanes and several other "relatively reactive" alkanes (16). This seemingly improbable happening resulted solely from the relatively large concentration of CH_4 relative to the other more reactive hydrocarbons cited. The extent to which CH_4, C_2H_6, C_2H_2, and the other hydrocarbons contributed to the O_3 generation for this day, however, was insignificant. Nevertheless, the example was cited to remind us that not only must we be concerned with the HO-rate constants and smog chamber reactivities, but obviously the amount of the RH present as well.

The point is made in this W.O.G.A. paper that there are no data showing that the slower reacting compounds are the prime sources of rural oxidant in transported, aged, urban air masses, and not the many other compounds present in the air mass, such as organic reaction products of the faster reacting compounds. Evidence that exists from the 1974 Midwest Study (19) and smog chamber results indeed show that aldehydes are a major product of the smog reactions. These species are known to initiate radical formation and can be important reactants for HO-radicals in aged air masses. To what extent the "unreactive" RHs and the aldehydes and the other compounds successfully compete for HO-radicals and help drive the NO to NO_2 conversion leading to higher ozone production, depends upon the relative magnitude of the concentration-HO-radical rate constant products: $k[CH_2O]$, $k'[CH_3CHO]$, $k''[RH]$, . . . It is possible that the aldehyde terms outweigh those for many of the unreactive hydrocarbons. So the point of this paper is not a trivial one, but can only be answered as better product analysis of the aged air masses are obtained. Each mixture needs to be considered in view of the composition. Generalizations from existing limited data are dangerous and unwarranted.

Major sources of a given light hydrocarbon mixture may result in the significant involvement of a given alkane. For this to occur, however, some primary radical source, not inherent in the presence of the alkane alone, must be present as well.

The W.O.G.A. placement of acetone in their "unreactive" Class I is surprising to me. The absence of acetone in the tables of Pitts et al. is also a surprise. I would imagine that it is at least as reactive as C_2H_6 and hence in Class II of the W.O.G.A. list. The new EPA chamber data (compare Table 3) show the acetone reactivity similar to that of butane and isobutyl acetate, therefore, in the W.O.G.A. reactivity Class III. This situation should be clarified by W.O.G.A.

"Application of Reactivity Criteria in Oxidant-Related Emission Control in the USA" by Basil Dimitriades and S. B. Joshi.

The authors discuss the occurrence of pollutant transport and smog chamber oxidant studies using various "unreactive" organics. They interpret the buildup of oxidant in old air masses in terms of the participation of "unreactive" hydrocarbons and conclude that there is a need for a new two-class reactivity classification of organic emissions.

It appears to be realistic to assume that if enough "unreactive" RH species is added to the atmosphere, it can participate in smog formation. When the product of HO-rate constant for the reaction of the "unreactive" hydrocarbon times the concentration of the "unreactive" hydrocarbon is greater than the same product for the reactive hydrocarbons, i.e.,

$$k_{\text{unreact RH}}[\text{RH}]_{\text{unreact}} > k_{\text{react RH}}[\text{RH}]_{\text{react}},$$

the significant participation of the unreactive hydrocarbon is assured, provided, of course, that there is some significant free radical source to initiate HO-formation. However the amounts of $[\text{RH}]_{\text{unreact}}$ required to cause comparable effects are large, in the ratio, $k_{\text{react RH}}/k_{\text{unreact RH}}$. For propane and propylene, for example, $15.1 \times 10^9/1.3 \times 10^9 = 11.6$-times as much C_3H_8 is required as C_8H_6 to have equal HO-attack rates in the atmosphere.

The authors are seemingly convinced that the direct atmospheric observation of reactivity-related control measures upon air quality is impossible. I am not so sure that we should come to this conclusion. Certainly smog chamber results are of very great value in controlling the variables and developing quantitative theories and reaction mechanisms of simple RH-NO_x dilute mixtures in air, but the ultimate test of these theories must include atmospheric testing. I believe that experimentation involving RH-NO_x mixture insertions into the real atmosphere can be designed to test current ideas related to oxidant formation. Since rules and regulations resulting from all of the studies will be applied to the real atmosphere and not to the control of smog chamber atmospheres, we must be careful to test the conclusions formulated from chamber experiments in the atmosphere before accepting these as completely applicable. This is particularly true in dealing with the unreactive RH compounds.

The real danger in using smog chamber results to assess the reactivity of the less reactive species is the unpredictable influence of the chamber walls on the laboratory experiments. It is not clear that the radical source attributed to the wall reactions has an equivalent counterpart in the real atmosphere. We know that the unreactive species do react slowly in the chambers, and it appears that by some unexplained mechanism HO-radicals have been produced to initiate this reaction. It is very important to recognize that the magnitude of this radical source may be much above that of atmospheric sources of HO-radical. The values of 1.5×10^7 to 1.7×10^8 molecules cc^{-1}, estimated from CH_4 removal experiments in the EPA smog chamber, are somewhat higher than those estimated in the Detroit atmosphere by Wang et al. (14) using resonance fluorescence measurements of HO (5×10^7 molecules cc^{-1}). However, they seem considerably higher than those estimated by absorption spectroscopy by Perner et al. (15) in Germany (4×10^6 to 7×10^6 molecules cc^{-1}), indirectly by Calvert (16) from relative RH removal rates in the LARPP experiments (4.5×10^6 to 0.5×10^6 molecules cc^{-1}), and estimated theoretically by our group (3×10^6 to 1×10^6 molecules cc^{-1}) (13) and by Crutzen and Fishman for the ambient air in the troposphere (0.8×10^6 to 1.5×10^6 molecules cc^{-1}) (20).

Note that if one makes the reasonable assumption that the rate determining step in the removal of the relatively unreactive species given in Table 1 of the Dimitriades and Joshi paper is in each case the attack of HO-radical on the species, then we can take the reported average rate of organic disappearance reported in the Table (% per hr), the estimated rate constant for HO reaction with the given RH (k_{RH}) and derive the average $[\overline{HO}]$ in the chamber:

$$[\overline{HO}], \text{ molec/cc} = \frac{(\text{Rate RH removal, \%/hr})(4.10 \times 10^{9})}{k_{RH}(\text{ppm}^{-1}\ \text{min}^{-1})}$$

Values calculated in this fashion for $[\overline{HO}]$ for all species for which the rate constant is known are shown in Table 3 (last column).

TABLE 3. ESTIMATED $[\overline{HO}]$ FROM EPA CHAMBER STUDIES OF ORGANIC REACTIVITIES

Compound	Rate(%/hr)	$k_{RH}(\text{ppm}^{-1}\text{min}^{-1})$	$[\overline{HO}]$, molecules/cc
CH_4	0.05	11.8	1.7×10^7
CH_3CCl_3	0.1	22	1.9×10^7
$CHCl_3$	0.8	61	5.4×10^7
C_6H_6	3.1	2083	0.6×10^7
CH_2Cl_2	5.7	206	11.3×10^7
Ethane	0.5	417	0.5×10^7
Propane	2.0	3185	0.3×10^7
Acetylene	6.3	242	10.7×10^7
n-Butane	1.4	4410	0.13×10^7
Methanol	1.3	1397	0.38×10^7
Methylethyl Ketone	1.5	4900	0.13×10^7
Isopropanol	3.3	10500	0.12×10^7

Several features of these data should be noted. The $[\overline{HO}]$ estimated varies over a factor of one hundred, from 1.1×10^8 using CH_2Cl_2 to $[\overline{HO}] = 1.2 \times 10^6$ molecules/cc in experiments with isopropanol. The highest of these estimates which appear with CH_2Cl_2 and C_2H_2 and the large variations

between compounds are not clearly understandable in terms of elementary rate data. It seems to me that the chamber data may not correspond to atmospheric rates, but the rates may be as much as a factor of 100 too high in some cases. Certainly one should exercise caution in the use of these chamber data to predict atmospheric happenings with the least reactive compounds.

A study should also be made in the chamber of the reactivity of carbon monoxide gas as well as the organic compounds. It is clear from previous studies (21-24) that CO may be classified as a "reactive" species in O_3 generation under some conditions.

In considering the uniqueness of the chamber walls for possible initiation reactions, one must include the reaction of HONO formation: $H_2O + NO + NO_2 \rightarrow 2HONO$. Heterogeneous generation of HONO at chamber walls may allow a unique source of HO radicals ($HONO + h\nu \rightarrow HO + NO$) in the chamber experiments. Although HONO may form homogeneously in the chamber and in the atmosphere, its rate through the homogeneous reaction, $H_2O + NO + NO_2 \rightarrow 2HONO$, is very low for the levels of NO, NO_2, and H_2O employed. Turbulent mixing in the chamber can be aided by thermal gradients within the operating chamber, and reactant contact with the walls can accentuate HONO formation and subsequent HO-radical generation. The analogous reactions may occur in the real atmosphere at ground level or on aerosols, but their importance is probably much less than in the smog chamber. Most HONO in the atmosphere probably arises from $HO + NO + M \rightarrow HONO + M$, and $HO_2 + NO_2 \rightarrow HONO + O_2$.

A further consideration is the possible significant deposition of CH_2O polymer on the chamber walls during these runs; it is a major product of the oxidation of most RH species. As the chamber wall is heated through the action of the lights, CH_2O evolution from the wall may occur to initiate radical generation and HO-radical attack on the RH:

$$CH_2O + h\nu \rightarrow CHO + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$CHO + O_2 \rightarrow HO_2 + CO$$

$$HO_2 + NO \rightarrow NO_2 + HO$$

$$HO + RH \rightarrow H_2O + R$$

In any case the nature of the initial source of the HO-radicals remains unclear, and it appears to me that the rates of removal of some of the unreactive RH compounds may be very much higher in the chamber than they would be in the atmosphere.

It is stated that the amounts of desorbed organics in the chamber are at immeasurably low concentrations at most. Immeasurable by what technique? Is the cell heated and evacuated between runs? Are blanks with clean air run periodically for extended periods? My experience with chambers suggests that the memory of the chamber for the previous chemicals employed can be very good, and it is very difficult to return to a clean chamber again without thorough heating, pumping, wall washing, etc.

The subtraction of O_3 created by irradiation of background air need not correct for the impurity influence, since the radicals formed from the initial impurity in an experiment with added unreactive hydrocarbon, can initiate long chains involving the "unreactive" hydrocarbon. These synergistic effects may be unique to the "dirty" chambers.

Of course reaction products such as CH_2O, CH_3CHO, HONO, etc., form in the atmosphere as RH oxidation occurs, and I would expect these species, as well as O_3, to initiate chain oxidation of the RH species in the atmosphere. The question that must be answered in the comparison of chamber and real atmosphere is whether the amounts of these compounds in the atmosphere are comparable to those released from the wall or formed at the wall in the chamber.

The conclusion that the existing classification of organics should be

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revised to reclassify most of the "unreactive" organics into a single class of reactives appears to me to be premature. Certainly we must understand the smog chamber and its apparent ill-defined sources of HO-radical before we can extrapolate its results to the atmosphere in any scientifically meaningful way. We must know the ambient levels of CH_2O, CH_3CHO, HONO, H_2O_2, O_3 and other potential photochemical sources of radicals in the atmosphere before we can make reasonable predictions concerning the reactivity of various RHs toward O_3 development in the atmosphere.

It is entirely reasonable that photochemically active radical sources exist in the atmosphere containing aged air masses. However the rate of ozone generation by these mixtures will remain unclear until the quantitative analytical information concerning their detailed chemical compositon is established and O_3 development in equivalent mixtures can be studied without the presence of unique radical sources peculiar to the smog chambers.

"Control Regulation for Stationary Sources of Hydrocarbons in the United States" by Robert T. Walsh.

The paper gives an accounting of the sources of the volatile organic compounds released to the atmosphere of the United States. The increase in the emissions from stationary sources, now at 60% of the total released into the atmosphere from all anthropogenic sources, is a concern in view of the possible influence of these compounds on photochemical oxidant formation.

It is stated on page 6 of the paper, "For oxidant control purposes, the program is aimed at reducing emissions of all volatile organic pollutants regardless of their photochemical reactivity." It appears to me that this is an extremely cautious approach that may involve considerable overkill. If excellent control is possible with little economic hardship, then the plan to eliminate all RH emissions is a very good one. I personally feel that the scientific evidence of rural oxidant formation does not warrant laws that eliminate all "unreactive" as well as "reactive" hydrocarbons at this time. The expenditure of some years of well planned research is necessary to estab-

lish the impact which such indiscriminant controls will have on oxidant formation. There is a good chance that little influence from the complete removal of "unreactive" hydrocarbons will be seen.

GENERAL CONCLUSIONS CONCERNING THE ISSUE OF REACTIVITY

The Question of the Borderline Separating Reactive Species from Those of "Virtually" No Concern in Oxidant Generation

The answers to the questions given in this section should be supplemented by reference to the discussion of the previous sections. The present laboratory and computer methods for evaluating oxidant-forming potential of organic compounds in the atmosphere all appear to have rather serious unevaluated problems related to their use. This conclusion is evident in the varied conclusions at which different workers arrive using these methods. It is, I hope, an accidential correlation that can be seen between the conclusions of the industrial researchers who find little influence from "unreactive" hydrocarbons on rural oxidant formation and the government supported researchers who feel there is a significant impact from these compounds. It appears to me that the judgmental flexibility and uncertainty in the evaluation methods now available make these conflicting conclusions inevitable.

It is highly unlikely that any one pure hydrocarbon will be the dominant ingredient in an RH-HO_x-polluted atmosphere, so the relevance of the ozone-forming potential in initially pure hydrocarbons in NO_x mixtures in smog chambers is not entirely clear to me. I believe we should be more concerned with the synergistic effects of added unreactive hydrocarbons on the common atmospheric contaminants present in rural and urban air masses. What emerges from the vast quantity of chamber data from NO_x-"unreactive" RH mixture irradiations are several rather quantitative measures of oxidant-forming potential of these mixtures in smog chambers. The applicability of these data to many cases in the real atmosphere remains unclear. Even the radical initiation steps as well as the HO levels present in chambers may not match well those present in rural and urban air masses.

To extrapolate the chamber data for computer models to the conditions present in the atmosphere, both EPA-supported scientists and industrial scientists have had to make certain questionable assumptions. Foremost among the problems is that of the seemingly artificially high [HO]-levels present in many of the smog chambers. The identification of the unknown initial driving force for the oxidation of pure CH_4, C_2H_6, C_3H_8, or n-C_4H_{10}, etc., in NO_x mixtures in chamber experiments is a scientific problem of large magnitude; its solution is of vital importance to the value of our extrapolations to the real atmosphere. It is possible that HONO and possibly some other species are contributors to this initial radical source, as many of the current workers assume. If this is the case, then we are quite sure that chamber data for the "unreactive" hydrocarbons will not relate well to their behavior in the real atmosphere. This is a consequence of the fact that HONO homogeneous development in the atmosphere, through the reaction $H_2O + NO + NO_2 \rightarrow 2HONO$, is extremely slow for the ambient levels of NO_x present. Although HONO must be formed in the atmosphere, it is probable that the reactions, $HO + NO + M \rightarrow HONO + M$, and $HO_2 + NO_2 \rightarrow HONO + O_2$, are its major sources here. If this is the case, the heterogeneous development of HONO, which may occur readily in a chamber, provides an unusual and atmospherically unrelated boost to the reactions of the "unreactive" species.

In the previous discussions of the papers in this review, I have indicated that two experimental estimates and several theoretical estimates of [HO] levels in the troposphere suggest that these are a factor of 1/10th to 1/100th of the levels estimated in present chambers. Another serious concern I have about chamber data is the undetermined effect of the NO_2-removal reactions, some of which are unique to the chamber. Thus $N_2O_5 + H_2O \rightarrow 2HONO_2$ reaction is probably only significant on the walls of the reactor. It is relatively unimportant in the atmosphere. When the [HO]-levels in chambers do not mimic well those in the atmosphere, then the formation of $HONO_2$ through the reaction, $HO + NO_2 + M \rightarrow HONO_2 + M$, and the attendant removal of NO_2 will not correspond to the atmospheric case, and obviously the O_3 formation pattern will be disturbed. In this regard it is interesting that the $[O_3]$-time profile seen in the Los Angeles Reactive Pollutant Program (LARPP) atmospheric study of the single air parcels shows a continuous rise of the $[O_3]$ during the

entire day of Nov. 5, 1973; there is no maximum in $[O_3]$ that is so characteristic of most smog chamber irradiations of auto exhaust. It is indeed a very risky business to use chamber data to extrapolate to the atmospheric conditions as they might apply to the "unreactive" hydrocarbons.

There appears to be a real uncertainty in view of the existing data as to whether the high rural oxidant is really developed significantly by the action of the unreactive hydrocarbons or whether new reactive hydrocarbon and NO_x insertions from natural and anthropogenic sources are the main stimulus to further O_3 development in aged air masses.

There is no question that working in consort with reactive hydrocarbons and oxidation products, the "unreactive" organics can participate in reactions leading to NO to NO_2 conversion and O_3 generation in the atmosphere. However, the important question that must be answered is: To what extent do these compounds increase the ozone levels in the aged mass ? The present data do not prove that the very high rural O_3 levels, sometimes observed, arise to any appreciable extent as a result of this involvement. It is equally true that the present data do not disprove this contention.

The results of chamber experiments and modeling available to me today do not lead to unambiguous answers as to which compounds are reactive and which are totally unreactive in the atmosphere. The classification of propane, butane, and all higher alkanes as class III compounds through their [HO] rate constants in the reactivity scale of Pitts et al. should not be taken as an indication that these compounds contribute significantly to O_3 development in aged air masses. If the [HO] level in the troposphere is 2×10^6 molecules/cc, rather than the 1×10^7 molecules/cc assumed by Pitts et al., then the halflives of these alkane species will be in the range of 5 to 0.5 days, and not 1 to 0.1 days as they suggest. Such relatively slow oxidations may not significantly increase the HO_2 and RO_2 radical levels above those created alone by the reactive oxidation products in the aged air mass, and hence they may not change the rate of NO to NO_2 conversion much and alter O_3 little.

Although the chamber and computer simulation experiments have given us a

great deal of useful information on the mechanism of smog formation, it is equally clear that there are significant differences between the chamber and the atmosphere. Thus, I feel that it is very important that we go back to the real atmosphere to answer questions that relate the subtle effects of "unreactive" hydrocarbons. Well planned atmospheric studies will answer questions about the atmosphere. If we wanted to control ozone levels in a given smog chamber, then the chamber data alone would suffice. If we knew well all of the critical rate constants and the precise composition of the urban and rural air masses, then the computer simulations would be of great value in formulating our strategy concerning reactive and unreactive hydrocarbons. As it is now, neither of these situations exists, although we seem to forget this now and then.

The Question Whether One Method or the Other or the Two Approaches Combined in Some Way or Some Other Approach Yields the Most Reliable Results

As outlined in the previous section, both chamber and modeling methods have serious problems related to their predictive value for the "unreactive" hydrocarbons. Obviously both techniques are valuable in principle, but existing problems and new unforeseen complications in their use are bound to appear as we look closely at these methods, making the unambiguous answers from either method impossible now. I honestly believe that EPA would be well advised to consider a third alternative, while the needed improvement in the other two methods is continuing. This alternative is the use of new direct atmospheric studies of the chemical changes in rural and urban air masses.

Specific Additional Research Needed

It appears to me that we need a great deal more information concerning the chemical composition of urban and rural air masses as a function of time before we can determine the reliability of the chamber data and computer studies in simulating the atmospheric problems. The cost of such studies need not be prohibitive if other federal agencies such as NASA, NBS, ERDA, NCAR, etc., would share their expertise and their financial assets in the project. If such experiments are to be meaningful they must be planned well to yield

the necessary kinetic and analytical data. Such plans will include unambiguous lifetime determinations through labeled compound injection, [HO] estimates in the atmosphere, etc.

We must identify the radical sources that stimulate the HO-chains and the oxidation of "unreactive" hydrocarbons in chambers. Good spectroscopic methods now exist that would seem to solve this problem easily.

It would be particularly embarrassing to us all and destructive to the EPA scientific efforts to the future if we proceed with the development of highly restrictive RH control measures from theory and chamber experiments at this time, and then learn that the real atmosphere is very different from what our simple picture had assumed. When it comes to the evaluation of the "unreactive" hydrocarbons, the present information of which I am aware is too contradictory and incomplete to reach a sound scientific judgment. I recommend strongly that we add an effort utilizing well planned field studies aimed at the role of "unreactive" hydrocarbons.

COMMENTS BY H.E. JEFFRIES

Dr. Calvert took a much broader view of the issues than I did in my review and came to a slightly different conclusion. We both question the relevance of ozone-forming potential of high concentrations of initially pure hydrocarbons in NO_x mixtures in smog chambers.

Although I agree with Dimitriades and Joshi that "it is not possible to directly assess the impact of reactivity-related solvent control by examination of air quality data ...", I do not disagree with Calvert's suggestion that "well planned atmospheric studies will answer questions about the atmosphere." Simple, fixed-state, ground-level air quality monitoring-type experiments are probably not what Calvert had in mind.

I suggested that smog chamber work and photochemical modeling must be used in combination if a clear understanding of the chemistry is to be ob-

tained; Calvert has reminded us that these are probably not sufficient to give unambiguous answers as to what the atmosphere does without actual atmospheric data to support the conclusions.

I have no major disagreements with Dr. Calvert's analysis.

REVIEW AND ANALYSIS

H. E. Jeffries

INTRODUCTION

Since 1971 the Environmental Protection Agency (EPA) has pursued an oxidant control strategy that focuses mainly on the control of organic emissions from mobile and stationary sources. The alternatives for hydrocarbon (HC) control are direct reduction of emissions, substitution of less "reactive" HCs for more reactive HCs, or some combination of both.

The concept of HC reactivity grew out of early smog chamber experiments in which different HCs were irradiated with oxides of nitrogen (NO_x) for fixed time periods. Different HCs gave rise to different ozone (O_3) or oxidant (O_x) levels at the end of the irradiation period. Thus, hydrocarbons were ranked according to their ability to produce O_3. Experiments carried out in different laboratories resulted in different absolute O_3 concentrations, but the relative rankings of HCs were in fairly good agreement. The experiments were primarily conducted at a HC to NO_x molar ratio of two, which was considered typical of urban centers, and for a duration of 6 hours. These data were reviewed and summarized at the International Conference on Photochemical Oxidant Pollution and Its Control by F. F. Farley (18).

In 1966 the Los Angeles County Air Pollution Control District implemented Rule 66 as a control measure for volatile organic solvents substitution based on photochemical reactivity as a means of reducing ambient oxidant levels. Similar regulations have been adopted by many jurisdictions, and industry has accommodated itself to these reductions and substitutions.

In its 1976 "Policy Statement on Use of the Concept of Photochemical

Reactivity of Organic Compounds in State Implementation Plans for Oxidant Control," EPA supported the positive reduction aspects of Rule 66 regulation, but questioned the utility of solvent substitution strategies based on more recent information on photochemical reactivity. This information grew out of investigations related to the so-called "rural oxidant problem," the finding of elevated O_3 (> 0.10 ppm) in areas relatively remote from urban centers in the Eastern part of the U.S. Thus "pollutant and oxidant transport problems" were introduced into the oxidant control strategy. Because of potential transport problems, the reactivity concept was reexamined and new smog chamber experiments were performed to measure reactivities under long irradiation times and higher organic-to-NO_x ratios (2).

These experiments suggested that almost all volatile organic compounds eventually reacted in the atmosphere to form some oxidant. Thus EPA's current policy changes tend toward positive reduction of all organic emissions except those that are shown to be *so little reactive that they would neither cause nor contribute significantly to oxidant buildup at problem levels under any circumstances*. This approach leads to a two-class reactivity scale: unreactive and reactive. Therefore, from EPA's viewpoint, the reactivity issue has become one of defining unreactive organic compounds. Dimitriades and Joshi (2) argue that the only method for identifying unreactive compounds is to conduct careful smog chamber experiments.

At the International Conference several papers dealt with the issue of reactivity. The EPA viewpoint was strongly challenged by Ford Motor Co. research scientists (3) on the basis of computer simulations of photochemical models and an analysis of aerometric data from a rural site. In addition, the General Motors Research Laboratories, on the basis of "multiday" smog chamber experiments, suggest that, in transport simulation experiments, HC reactivity is "only moderately altered on the second and third days of irradiation and, thus, hydrocarbon reactivity is still an important consideration in controlling organic emissions even in situations involving long-distance transport" (11).

Farley (18), representing the Western Oil and Gas Association, in his

review of previous smog chamber reactivity studies, recognized the possibility of slower reacting compounds participating in oxidant formation under transport conditions, but was not convinced by existing evidence that these caused much increase in oxidant compared to the organic reaction products of faster reacting compounds. He also said that if the slower reacting compounds are significant precursors to oxidant, then the utility of a reactivity scale based on O_3 formation in (older) smog chamber studies would be diminished.

Pitts et al. (25) suggested an alternative to smog chamber experiments as a means of assessing reactivity. Smog chamber experiments, they noted "would be extremely time consuming and expensive and would inevitably suffer to some degree from the problems noted in previous chamber studies of this type." Instead, they propose a "supplementary (rather than a substitute) approach in obtaining the required data." This approach consists of a hydrocarbon reactivity scale based not on secondary smog manifestation criteria (that is, O_3 formation), but rather on the primary chemical act of hydroxyl radical (OH) attack on organic species. Two reasons were given: OH is the most important reactive intermediate, and this approach can identify those compounds that particpate at "significant" rates in atmospheric reactions. Chang and Weinstock also took exception to this OH reactivity scale on the basis that it over predicts the reactivity of less reactive HCs compared to more reactive HCs.

The purpose of this review is to critically examine the reported evidence and viewpoints for conflicts, to make judgments on the strengths and weaknesses of opposing viewpoints or evidence, to attempt a reconciliation of these conflicts, to derive factual or judgmental (referee) conclusions regarding resolution or status of the issue, and finally, to offer recommendations for additional research.

The central aspects of this issue are embodied in the evidence and arguments presented in the Dimitriades and Joshi paper and in the Chang and Weinstock paper. Therefore, these two papers will be reviewed extensively. Other sources of information will be drawn upon as needed.

DISCUSSION

Areas of Conflict

Dimitriades and Joshi make several arguments of a philosophical nature. It is not possible to directly assess the impact of reactivity-related solvent control by examination of *air quality data* because any impact is masked by the overwhelming effects of other factors such as auto exhaust emission reduction and other effects. This impact must therefore be assessed *indirectly* based on laboratory evidence; direct atmospheric observation is *inconclusive*.

The relative roles of "reactive" and unreactive" organics, when they are subjected to pollutant transport conditions, likewise, can only be examined indirectly based on laboratory evidence. Relative contributions of the reactive and unreactive organics to ambient oxidant cannot be determined from aerometric data.

Chang and Weinstock, in support of their argument that the less reactive, "leftover" HCs were not responsible for rural O_3, but that "fresh" emissions of both NO_x and HC from local sources were responsible, carried out an analysis of aerometric data from the summer rural area study of 1974. They stated that the importance of "leftover" HCs compared to "fresh" HCs can be deduced from detailed measurements of rural HC, in that, if "leftover" HCs from urban areas are present in significant quantities, this should be evident by an accumulation of less reactive species compared to more reactive ones (i.e., a fractionation process). They did not find any evidence of such fractionation and thus assumed that local sources rather than transport was the main source.

They also interpreted HC and O_3 vertical profiles at three times during a single day at Wilmington, Ohio, to support their theory that the O_3 observed at this "rural" site was the result of buildup of new nonmethane hydrocarbon (NMHC) under the inversion layer. Thus they contend that rural O_3 is the result of reactions of "fresh" HCs and NO_x emitted into the mixing layer and "leftover" HCs play only a minor role in augmenting this increase.

Hence, Dimitriades and Joshi claim that aerometric data cannot be used to assess the role of "reactive" and "unreactive" organics and Chang and Weinstock claim to have done exactly this.

Dimitriades and Joshi continue their argument as follows. Laboratory evidence was interpreted to mean smog chamber evidence. It was recognized that there are uncertainties arising from the indirect nature of smog chamber experiments, but this approach was considered to be the only basis for reassessing the use and utility of the reactivity concept.

Chang and Weinstock express a viewpoint that smog chamber data is misleading with respect to oxidant reactivity. Some of the basis for this conclusion was presented in their Conference paper, but more information appeared in Weinstock and Chang (26) and in Niki and Weinstock (27). The details of this argument will be discussed later; the following is a brief summary of their position:

> Chang and Weinstock believe that smog chamber studies generally make less reactive compounds appear to have an anomalously high photochemical reactivity compared with more reactive compounds because of the existence of a substantial hydroxyl (OH) radical background in smog chambers. It is this OH background that drives these unreactive systems and not the inherent reactivity of the HC. Therefore, the behavior of HC in smog chambers is not representative of their atmospheric behavior. No specific cause of the OH background was given, but it was implied that it arises from material that is not removed during the usual cleanup of the chamber.

In their paper, Dimitriades and Joshi stated that although the above claim (that there may have been an OH background in the EPA chamber of comparable or slightly higher magnitude than that observed in the ambient atmosphere at Ford research laboratories) might have been qualitatively correct, this did not invalidate the original interpretation of the smog chamber data. That is, under optimum conditions many of the thought-to-be unreactive organics can, in fact, cause significant O_3 buildup. They argue that:

- OH formed from photolysis of nitrogen compounds desorbed off walls is unlikely to be important relative to the source created by the NO_x reactant itself.
- OH could form from photochemical reactions of wall-desorbed organics and the NO_x reactant, but such organics are at such almost immeasurably low concentrations that this source must also unavoidably be present in the real atmosphere as a natural background contamination.
- Any bias caused by a background OH source can be reduced — but not eliminated — by subtracting from measured reactivity values the background air reactivity.
- Irrespective of chamber background OH problems, it has been shown that conditions of prolonged irradiation and an optimum organic-to-NO_x ratio do enhance the reactivities of the less reactive organics.

They also proposed and illustrated a procedure for determining the borderline between unreactive and reactive organic compounds that consisted of obtaining smog chamber data in an appropriate chamber under optimum irradiation time and organic-to-NO_x ratio conditions. A compound that would not produce more than 0.08 ppm O_3 would be declared unreactive. Only the least reactive organic would have to be tested. No definition of appropriate was given. The illustrative data, which were obtained at 4.0 ppm organic and 0.2 ppm NO_x initial conditions in constant light intensity (Φk_a for NO_2 = 0.33 min^{-1}) irradiations lasting up to nearly 14 hours, suggested that the borderline was at propane. It was indicated that the test conditions might not have been optimum.

Chang and Weinstock used computer simulation of a Ford Research Staff derived photochemical model (FPM) to challenge Dimitriades and Joshi smog chamber results. The following approach was used. Chang and Weinstock discounted the results obtained by Dimitriades and Joshi for the propane/NO_x system (EPA Run 194) because, first, the results were not in agreement with those from the FPM (2 pphm for the model versus 11 pphm for the chamber), and second, major modifications involving nitrous acid (HONO) productions, increased O_3 heterogeneous loss, and NO_2 heterogeneous conversion to nitric acid

(HNO_3) were required to obtain a reasonable agreement between the FPM and the smog chamber data. Chang and Weinstock indicate that similar results were also found for the ethane smog chamber data of Dimitriades and Joshi. In using the modified FPM, Chang and Weinstock found general agreement with smog chamber data by Heuss (28) for ethane (0.08 ppm O_3), propane (0.13 ppm O_3), and butane (0.20 ppm O_3) thus implying that most smog chambers share the same problems and that the FPM model had captured the essence of this problem. They applied the unmodified model to simulate a rural situation having various low levels of propane and NO_x and based on the results suggested that propane would not generate elevated levels of rural O_3.

The Chang and Weinstock approach is essentially a proposal to substitute photochemical modeling results for smog chamber results in that an assumption was implicitly made that the Ford photochemical model had greater validity than the smog chamber data.

Thus, there are several specific areas of conflict presented in the two papers with supporting data frequently cited. These areas all touch upon the utility of smog chamber data. Dimitriades and Joshi's position is that, even though smog chambers have some problems, they are the only method available. Chang and Weinstock believe that, based primarily on photochemical model predictions, the technical basis of proposed reactivity policy changes is highly questionable.

Comments on Strengths and Weaknesses

Use of Aerometric Data

The first viewpoint of Dimitriades and Joshi is essentially obvious. So many important factors have changed in Los Angeles since Rule 66 was implemented that it *is not* possible to assess the benefits that may have occurred. Their second proposition is considerably more difficult to judge in light of Chang and Weinstock's suggestion that relative distributions of HCs in rural areas be examined. Pitts et al. (25) in their paper suggest that the half-life for the less reactive alkanes is between 0.1 and 1 day with most of them

falling nearer the 0.1 side of the interval. Thus significant consumption of even the less reactive HCs might be expected as opposed to accumulation as suggested by Chang and Weinstock.

Lonneman (29) in his analysis of detailed HCs samples from Wilmington, Ohio, suggested that 74% of the total NMHC was due to vehicular tailpipe emissions. In addition, he presented data to show that the Wilmington, Ohio, sample generally indicated reduced olefin and aeromatic content. He concluded that the samples taken at Wilmington represented diluted urban HC mix with associated photochemical loss of the more reactive compounds during the transport process. This conclusion directly contradicts that of Chang and Weinstock.

With respect to the vertical profile data for Wilmington, Ohio, I find the arguments advanced by Chang and Weinstock weak in certain aspects. First, whether the higher NMHC in the lower levels is due to "fresh" sources or not can only be determined by an examination of the detailed HC distribution and this was not given. Second, since significant time elapsed between soundings and no wind speed information was given, it is not possible to assume that the morning conditions gave rise to the afternoon O_3 observed unless spatial uniformity is also assumed.

Overall, the Dimitriades and Joshi viewpoint concerning the utility of aerometric data are probably correct; however, supporting information may possibly be obtained by careful analysis of detailed HC data; it probably will not be conclusive.

Use of Smog Chamber Data

The smog chamber has played a central role in developing an understanding of photochemical smog; it is not without its problems, however. Table 1 gives some of the characteristics of smog chambers as an investigative tool. The smog chamber's greatest attribute is that it is capable of producing observations of actual chemical events, limited only by availability of suitable and accurate analytical methods. The smog chamber's greatest weakness is that it has walls that can potentially influence the outcome of the chemistry (see

TABLE 1. COMPARISON OF SMOG CHAMBER AND COMPUTER SIMULATION METHODS

Smog Chamber Experiments	Computer Simulation of Mechanisms
1. Observations of physical and chemical events.	1. Theoretical descriptions of chemical and physical processes, and the behavior of these processes at selected conditions.
2. Observations are usually limited to only a few aspects of the total system because of absence of analytical methods, lack of instrument sensitivity, or costs associated with the more sophisticated analytical methods (GC/MS, LPIR/FTS, laser flourescence spectroscopy). Data can be obtained for any organic compound which can be analyzed.	2. Model is limited to processes that are know and reasonably well understood. Models are thus limited to those systems for which a reasonable mechanism has been identified and tested (paraffins and olefins).
3. Observations are error-prone, that is, accuracy and precision limited by analytical methods (calibration, specificity of instrument response, and minimum detectable concentration).	3. Theory is based on laboratory observations. These observations, however, come from a large range of experimental systems and are correlated with other fundamental data. The theory rests primarily on small scale, isolated-reaction-type, kinetic measurements supplemented by thermochemical theory and calculations. Only a small amount of the theory depends upon smog chamber data. This data base is far from ideal in that many rate constants and quantum yields for photolysis have relatively large uncertainty factors (2-5) and major errors may be associated with product identity and yield for organic degradation reactions. In addition, some inorganic radical reactions also have uncertain products.

(continued)

TABLE 1. (Continued)

Smog Chamber Experiments	Computer Simulation of Mechanisms
4. Requires a physical facility which, with its associated instrumentation, requires a great deal of maintenance and skill to obtain consistent results; that is, results may have a good deal of variability.	4. Requires a large data base and produces a very large amount of information. There are recognized solution techniques for mechanisms that produce essentially error free simulations of the descriptions given, that is, results can be made to have a large degree of numerical precision. Accuracy, however, is subject to the correct choice of a mechanism and its parameters.
5. Chemical processes under observation potentially include undesirable processes such as heterogeneous reactions involving the surface of the chamber (material is lost to walls, and some reactions proceed by a surface mediated path), and the introduction of reactants from the surface into the gas (off-gassing) which may influence the chemical reaction pathways and thus influence the observations. Many kinds of chamber characterizations tests are required to assess these undesirable processes.	5. Because of the absence of concentration information, which hinders speculation on the types of mechanistic sequences needed, it is difficult to express the "chamber characteristics" in terms of known reactions. This reflects a general lack of understanding of the "background process" more than any shortcoming on the modeller's part.

(continued)

TABLE 1. (Continued)

Smog Chamber Experiments	Computer Simulation of Mechanisms
6. Although the situation has greatly improved, many parameters of importance (intensity, spectral and spatial distribution of light source, temporal variation in these factors, temperature, purity of background air, and humidity) are still frequently not measured or controlled. In older studies the importance of these factors was often not recognized and no information exists for these parameters.	6. The modeler must have a value for every parameter in model. If these are not known, then he must guess at a value.
7. Difficult to derive analytical expressions or to investigate the causative processes responsible for a given outcome from the usual observations made in experiments. It is also difficult to extrapolate to non-experimental conditions.	7. Easy to determine those components of a mechanism which give rise to an outcome. Only tool for manipulating a mechanism. If it is assumed that the mechanism has captured the essence of the chemical process under study, then it is easy to extrapolate to non-experimental conditions.
8. Sensitivity analysis difficult.	8. Sensitivity analysis easy.

Table 1, item 5). It is to this area that Chang and Weinstock direct their strongest criticism.

The term "dirty chamber effect" was coined by Bufalini et al. (30) to describe the significant NO-to-NO_2 conversion rates obtained in smog chamber irradiations without the addition of HC to the system. They were able to prevent this conversion by washing the walls of their glass reactor between runs. This term is also used to describe the formation of O_3 in irradiation of ultra-high purity air. An example of this process is shown in Figure 1 (this is the chamber used by Dimitriades and Joshi).

Chang and Weinstock make the claim that the "dirty chamber effect" is due to generation of OH and hydroperoxy (HO_2) radicals from background contamination during irradiation and that this source is of overwhelming magnitude compared to the hydrocarbon related sources. They base this argument on the following evidence.

In experiments conducted in their chamber ("dry glass chamber"), NO at 0.95 ppm decayed very slowly when irradiated ($t_{1/2} \simeq 512$ mins), thus illustrating the purity of the background air, but when CO was added at high concentrations (110 and 665 ppm) the NO decay was greatly increased ($t_{1/2} = 89$ and 22 mins) thus illustrating that OH was involved because CO is an efficient converter of OH to HO_2:

$$OH + CO \xrightarrow{O_2} CO_2 + HO_2$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

No explanation was offered as to the actual source of this OH other than small contaminants in the system.

Ford research scientists had measured OH in ambient air outside the Dearborn laboratory by a pulsed laser fluorescence method. The uncertainty of OH concentration by this technique was given as about a factor of 3 and the

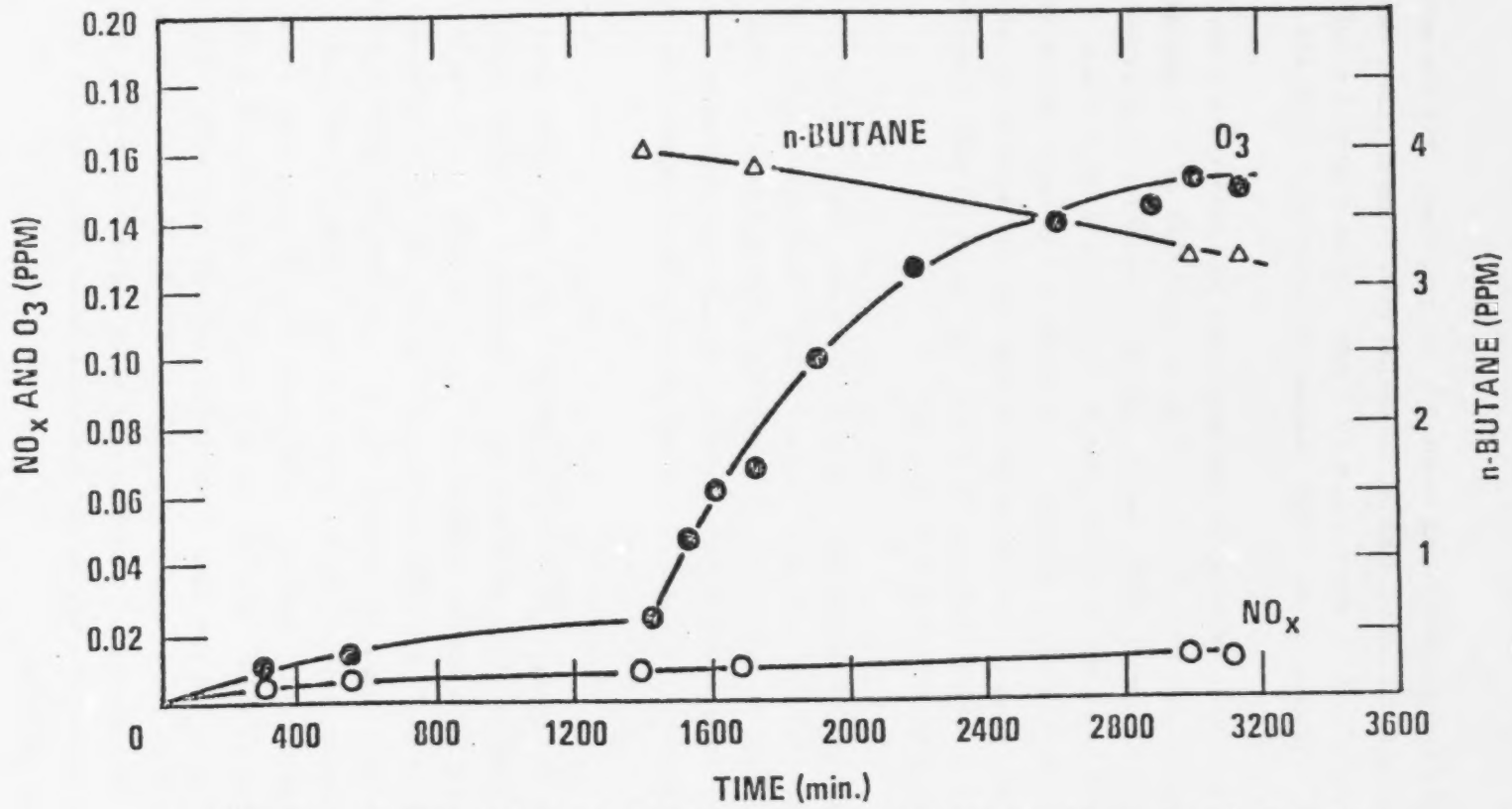

Figure 1. "Ultra Clean" air irradiation in cylindrical 400-liter glass/teflon EPA chamber. Chamber air was initially recirculated for 16 hours through activated charcoal, heated 0.5% rhodium on 1/8-inch alumina pellet catalyst, purafil, and activated charcoal. The air was then ozonized (1 ppm O_3), held 6 hours in dark, and finally recirculated as initially for 16 additional hours. Initial conditions at start of irradiation: NO_x < 1 ppb, O_3 < 1 ppb, total HC < 50 ppb. N-butane injected at 1400 minutes (33).

minimum detectable concentration was about 2×10^{7} ppm (14). The atmospheric measurements showed significant diurnal variation with maximum values near 2.4×10^{-6} and average values of about 1.2×10^{-6} ppm. Ozone measured simultaneously, however, was only 30 to 70 ppb indicating relatively clean air.

A check on the laser calibration was performed by irradiating propylene/NO_x mixtures at high NO-to-NO_x and NO-to-HC ratios so as to suppress O_3 formation. Hydroxyl concentration was deduced by calculation from propylene concentrations and the known rate constant for propylene + OH reaction. These calculations gave a value of 5.26×10^{-7} ppm OH while the laser method gave 6.1×10^{-7} ppm OH. A photochemical model of this system, however, predicted OH concentrations an order of magnitude lower. It was concluded, therefore, that there was a large background source of OH.

Long path infrared/FTS spectra of the Ford chamber, when filled with clean air, showed [HNO_3] = 0.14 ppm, [formic acid] = 0.08 ppm, [H_2O] = 8 ppm, and [CO] = 0.14 ppm. It was stated that HONO had been observed in other studies, but they did not state the circumstances nor the magnitudes. These were considered potential sources of OH, but a mechanistic explanation was not offered.

An estimate of the average OH during methane (CH_4)/NO_x experiments in Dimitriades and Joshi's glass smog chamber was made from the disappearance of CH_4 during the 1500-1900 minute irradiation time. Methane concentrations decayed from 4.0 to 3.45 ppm (1880 mins) and from 3.6 to 2.8 (1500 mins). These values included sampling loss and CH_4 was measured with a Beckman 6800 environmental chromatograph. Stating that they had corrected the final CH_4 values for sampling losses, Weinstock and Chang (26) calculated an average OH concentration of 6.07×10^{-7} ppm for the 1880 min, 4.0 ppm run and 6.88×10^{-6} ppm for the 1500 min, 3.6 ppm run. They indicated that the first value is near that measured in the atmosphere, but the second is an order of magnitude greater. Thus, they concluded that there is an OH background source in the EPA chamber that drives the system and therefore makes less reactive HCs appear to be more reactive.

Finally, there was major disagreement between Dimitriades and Joshi's chamber results and a photochemical model derived by Chang and Weinstock. This point will be discussed in detail later.

Although there certainly is some type of "dirty chamber effect," and although Chang and Weinstock may be correct in their hypothesis that there is a chamber background of OH, there are several weaknesses in the evidence presented. For example: in the NO decay experiments, although it is clear that OH was present, it was not clear that the source was the chamber walls. The irradiation of NO in air alone does not demonstrate the purity of the background air in that, if there is no material to serve as an OH to HO_2 converter, the dominant reactions, given an existing gas phase OH source, would be:

$$OH + NO \rightarrow HONO \qquad k = 1.2 \times 10^4 \text{ ppm}^{-1}\text{-min}^{-1}$$

$$HONO \rightarrow NO + OH \qquad k = 0.18\ \phi Ka \text{ for } NO_2$$

$$OH + NO_2 \rightarrow HNO_3 \qquad k = 1.5 \times 10^4 \text{ ppm}^{-1}\text{-min}^{1}$$

Thus, there could have been a source of OH in the background air, and it would not have been detected. Since no details were given, it is difficult to assess the homogeneous and heterogeneous process

$$NO + NO_2 + H_2O \rightleftarrows HONO,$$

but it was stated that the reactor was "dry." Acceleration of NO conversion on addition of CO indicates that OH is present; it does not indicate where the OH originates.

It has been suggested that the OH concentrations measured by Wang et al. (14) are too high because too broad a laser pulse was used (Whitten and Hogo, (43), who cited a personal communication between D.D. Davis and M. Dodge in 1976). Davis et al. (31) have also measured much lower OH concentrations in the troposphere than those reported by Wang et al. The OH concentrations reported do seem to be quite high in that associated NMHC were below 10 ppb,

CH_4 was at its background level of 1.55 ± 0.05 ppm, CO was approximately 0.5 ppm, NO was 3 ppb, and NO_2 was 20 ppb. Using an average peak value of 2.4 x 10^{-6} ppm OH, which lasted from 1.5 to 3 hours, the half-life for propylene would only be 7.5 minutes (using average OH values, approximately 15). The CO half-life would be 648 minutes, and cis-2-butene would have a half-life to only 4 minutes. These are extremely short times and cast doubts on the representativeness of the measurements.

Chang and Weinstock report good agreement between the laser measurements and estimates calculated from the rate constant for OH attack on propylene, but these were an order of magnitude higher than those predicted by a photochemical model. The rate constant for OH + propylene has recently been revised upward by a factor of 1.5 to 3.8 x 10^4 ppm^{-1}-min^{-1} (31,25,32). Estimating a half-life for propylene of 80 minutes from the graph of this experiment and using the new rate constant, I obtained an average [OH] of 2.28 x 10^{-7} ppm, almost a factor of three less than the measured OH. With respect to the disagreement between the OH predictions of the photochemical model, the question that must be asked is: did the model predict the propylene concentration-time profile? If it did, then either there is something wrong with the model or there is something wrong with estimating OH from HC decay. If it did not predict the propylene decay then there is clearly something wrong with the model. Other modelers (43) have had little difficulty obtaining excellent agreement between photochemical model propylene predicted values and actual chamber propylene data. Their OH predicted values, however, are less than those measured by Wang et al. (14). It should be noted, that aldehydes formed from products of the OH attack photolyze to produce HO_2, which is converted to OH by HO_2 + NO → NO_2 + OH. The quantum yields for aldehyde photolysis are strongly dependent on wavelength and are also uncertain, leading to modeling difficulties. This source may also account for the calculated OH concentration in this system.

The photolysis of HNO_3 in the gas phase is very slow making this a poor source of OH. ($\Phi Ka \simeq 3 \times 10^{-4}$ min^{-1} in fluorescent lamp illuminated chamber having a ΦKa of NO_2 = 0.3 min^{-1}, Bufalini et al., (33).) Bufalini et al., however, suggested that HNO_3 may undergo a bathochromic shift in the absorp-

tion region due to its absorbed state, leading to a higher rate of photolysis. Formic acid does not absorb UV light at wavelengths greater than 240 nm (34) making it a poor source of OH. On the other hand, Figure 1 makes it clear that there is some nitrogen compound absorbed on the walls that is capable of giving a response to the chemiluminescent NO_x meter and leading to O_3 production. Therefore, unless Bufalini's hypothesis is correct, Chang and Weinstock's observations are not conclusive in explaining the cause of the "dirty chamber effect."

In the CH_4 data reported by Dimitriades and Joshi, the ratio of final-to-initial CH_4 was 0.862 and 0.778. These values included sampling losses over the 1500 to 1900 minute exposure period. Chang and Weinstock state that they corrected these values for sampling losses. I back calculated from the rate constant for OH + CH_4, the time, and the calculated OH values of Chang and Weinstock to obtain the loss due to OH. These values were 1.33% loss in the 1830 minute run and 11.43% loss in the 1500 minute run. The environmental chromatograph has at least ± 0.05 ppm noise on the signal (1.25% of 4.0 ppm) and the sampling represents part of the loss (factor of 10 in first case, and factor of 2 in the second case). Thus, a small error in reporting the sampling rate or in the total time of sampling could lead to substantial errors in estimating CH_4 loss due to chemistry. Therefore, the accuracy of the estimated OH is probably very poor (perhaps by a factor of 10).

Thus, it appears that much of Chang and Weinstock's evidence for an overwhelming OH background source is of an uncertain nature primarily because they can not offer a reasonable explanation for the origin (Bufalini may have, but this remains to be tested), nor are their measurements of OH concentration consistent with other data; therefore, it is difficult to conclude that OH concentrations in chambers are greatly different from those in the atmosphere.

Dimitriades and Joshi's counterarguments, however, are also somewhat weak and based more on intuition than on factual evidence. For example, the argument that OH formed from nitrogen material desorbed off the walls is unlikely to be important relative to the source created by the NO_x reactant itself can only be true if substantial initiating sources are included in the

gaseous chamber charge, such as a few tenths of a ppb of HONO or a few ppb of aldehyde. It may well be that NO_x cannot be injected into chambers without forming some HONO, but since the levels required cannot be measured, one cannot tell whether the material is in the air or comes off the walls. If Bufalini's spectral shift for HNO_3 is correct, then it would be difficult to distinquish between 0.1 ppb gas phase HONO and OH + NO_2 from photolysis of HNO_3 on the walls.

The initial source of OH is *very important*, because, once OH is formed, propagation and chain branching steps can rapidly increase the concentration. Alkanes, for example, (according to current theory) are converted into aldehydes subsequent to OH attack while preserving the original radical (as HO_2). Photolysis of the aldehydes then introduces two new radicals that, in the presence of NO_x, leads to more OH. Without some initial source, the system may be so rate-limited in generating OH or HO_2 sources that no significant conversion takes place.

It is clear from background runs such as Figure 1 that some nitrogen containing source capable of providing NO_2 *and some source of radicals capable of converting NO to* NO_2 is probably associated with smog chamber walls. The entity that is oxidized in converting OH back to HO_2 is a major unknown. *The question that must be answered is: what is the relative importance of these wall-associated processes with reasonable* NO_x *concentrations and organic material?* If it is not possible to inject NO_x into a chamber without forming 0.1 ppb of HONO, then it seems unlikely that atmospheric emissions of NO_x would be completely free of HONO (10).

The presence of two initial sources of OH radicals is not additive in their impact. For example, Demerjian et al. (5) in their modeling study compared two simulations of HC/NO_x system having initial aldehydes. In one simulation the rate constants for HONO equilibrium with NO, NO_2, and H_2O were set to zero thereby removing an initial source of HONO. Also the rate constant for HNO_3 formation by N_2O_5 and H_2O was made zero. In the second simulation, these rate constants were assigned what are now considered to be large values, thereby providing a relatively large source of HONO almost immediately.

There was almost no difference in time to NO_2 or NO_2 maximum, but O_3 was 0.03 ppm lower when HNO_3 formation from N_2O_5 was allowed. The second simulation was repeated with HONO pre-equilibration assumed (i.e., initial HONO was present at 5 ppb). Again there were only small differences: 22 minutes to NO_2 maximum versus 24 minutes for simulation 2 and 31 minutes for simulation 1. An examination of radical sources showed that the OH and HO_2 flux had been approximately doubled between simulation 1 and 3. The aldehyde photolysis reactions were major radical sources in all three cases.

Thus the applicability of results obtained during clean air irradiations to regular run results with HC and NO_x present may depend upon whether NO and NO_2 can be injected into a chamber without forming small concentrations of HONO (< 1 ppb). Thus, the need of the modeler to add a few tenths of a ppb of HONO initially in his model is not necessarily an indication of a "dirty chamber effect."

Finally, the real atmosphere is not free of OH sources, and the emission of the compounds of interest are not likely to occur in a total pure state; therefore, as suggested by Dimitriades and Joshi any "boost" given to the chemistry in a smog chamber with as low a background reactivity as the EPA chamber *is* likely to be less than what would occur in the atmosphere.

Use of Photochemical Models

Computer simulation of photochemical models (modeling) has become a major research tool providing a kind of understanding and insight that is almost impossible to obtain otherwise. The application of models and the generation of the fundamental kinetic information necessary to support the models are very active research areas, and, consequently, the mechanisms used in the simulations are constantly in a state of flux. The trend of this flux has generally been toward improved predictions and greater understanding. Unfortunately, this constant revising and updating has led some to be overly suspicious of modeling efforts, and it has made it difficult for everyone to keep up with the latest information.

Table 1 gives some of the attributes of computer simulations of photochemical mechanisms. The strongest attribute is its ability to combine a great deal of theoretical information into a unified result. It is ideal for testing various hypotheses about mechanisms. The greatest shortcoming of modeling is in the data base: precise and accurate values of rate constants, product identity and yields, and the uncertainty that all reactions of importance have been found and quantified.

Modeling and smog chamber experimenting are highly complementary. When one models a particular run, the question being asked is: *are the observations made during one experimental run consistent with known theory as expressed by the model mechanism used?*

If there is close agreement between experimental observation and model predictions it simply means that there is agreement for this particular run. This does not mean that the observations and the model are correct. Since there are many choices in constructing a mechanism (different interpretations of theory), the agreement may be coincidental. Agreement at other conditions may be very poor.

If there are substantial differences between experimental observation and model (theory) predictions the source of disagreement may be in the observations, in the theory, or in both. The observations may include the influence of a process that was not intended to be present (and therefore, not included in the model, e.g., wall-related processes), or operational parameters (such as spectral distribution) may actually have been different from what they were thought to be (and from the representation used in the model). Analytical errors could have contributed significant differences ($[O_3]$ high by 35% due to calibration errors).

Alternatively, the theory used to establish the mechanism could be substantially wrong: rate constants have been revised by more than a factor of three, a reaction was written with wrong products, or the representation of the theory used in the model introduced a model artifact (use of "lumping" or steady-state assumptions where not appropriate).

Ultimately, a disagreement between experimental observation (assuming the absence of significant analytical errors) and theory as expressed by the mechanism simulation results must mean that the theory (as expressed) is wrong, since *the chemical events actually occurred*. Not being able to account for the experimental outcome, however, is a very uncomfortable position, since it may mean that the observations do not represent what was intended.

A major component of the argument presented by Chang and Weinstock at the International Conference was based on a comparison of their photochemical modeling results with Dimitriades and Joshi's chamber results. Because there was substantial disagreement between their initial model and the EPA chamber results and because substantial modifications in the form of heterogeneous type changes were required to obtain agreement, they concluded that Dimitriades and Joshi's, and Heuss' smog chambers had important "idiosyncrasies."

Although it may be possible that Chang and Weinstock are correct in their conclusions about the EPA chamber, the discussion given above suggests other alternative interpretations. This is especially true in light of other smog chamber data and modeling results for propane.

On September 8, 1976, the Research Triangle Institute (RTI) carried out a 4.0 ppm propane, 0.16 NO_x, 0.032 ppm NO_2 run in one of their 1000 ft^3 outdoor Teflon chambers. These chambers were described in a paper by Sickles et al. at the Conference (35). Following the outcome in this experiment, six simultaneous similar propane experiments were performed on September 20, 1976, involving the four 1000 ft^3 RTI outdoor chambers and the dual 5500 ft^3 (each side) University of North Carolina outdoor chambers.

September 8, 1976, was the hottest day of the month (maximum air temperature > 90°F while September 20 was cooler (air temperature 82°F) with increasing cloud cover all day (6/10 by 1600 EDT). The September 8 run had a maximum O_3 of 0.61 ppm while the six runs on September 20 had an average value of 0.211 ppm O_3 with a standard deviation of 0.027 ppm (these values include the effects of not having identical initial conditions in all chambers but

include O_3 calibration corrections). The maximum occurred at the same time in all six chambers (36).

To investigate the high O_3 yield in the RTI September 8 run, Dr. Marcia Dodge, Environmental Protection Agency, Research Triangle Park, modeled the run (memorandum from M. Dodge to J. Bufalini, October 15, 1976). In these simulations, an effort was made to duplicate the actual conditions closely: diurnal values of the photolytic rate constants corresponding to September 15 for 40°N latitude (RTI is at 36°N) were used; rate constants for reactions having significant activation energies were computed at 85°F; the observed dark decay rate of 4.5×10^{-4} min^{-1} for O_3 was used; lastly, the rate constants for processes normally associated with heterogeneous loss processes were assigned *low* rate constants (homogeneous limits). Two factors were considered "unknown": the levels of impurities in the "clean air" and the rate constant for OH + propane. Therefore, some initial HONO was assumed to be present due to reactions of NO, NO_2, and H_2O (injections occurred several hours before sunrise). Values of 0.1 and 0.2 ppb HONO were chosen. Also formaldehyde and acetaldehyde were assumed to be present in equal amounts at total concentrations of 1 or 4 ppb. Two values of the rate constant had been reported at the time of this work: Greiner reported 2.2×10^3 ppm^{-1}-min^{-1}, and Volman more recently reported 3.2×10^3 $ppm^{-1}min^{-1}$. Pitts et al. (25) give a value that agrees with 3.2×10^3 ppm^{-1}-min^{-1}.

The comparison results are given in Table 2. Using 0.2 ppb $[HONO]_o$ and 4 ppb $[aldehyde]_o$ and Volman's rate constant, a value of 0.61 ppm O_3 peak occurred at 4:00 compared to the chamber time of 4:18, and the chamber NO-NO_2 crossover occurred between 10:00 and 12:00 compared with the model value of 11:30. Dodge states, "Thus, it is not necessary to invoke chamber contamination effects to explain the results, if one assumes that the higher propane + OH rate constant is correct and if one assumes that the NO_x loss is a minimal as was used in the model" (memorandum from M. Dodge to J. Bufalini).

Dodge also applied her model to a "rural" situation; using LA summer solstice photolytic rate constants and removing the O_3 dark loss reaction, she repeated the simulation for one tenth the RTI values. The results are given

TABLE 2. COMPUTER SIMULATION RESULTS FOR THE SEPTEMBER 8, 1976 RTI OUTDOOR SMOG CHAMBER PROPANE AND NO_x EXPERIMENT (FROM DODGE, 1976)[a]

$[NO_x]_0$ = 0.16 ppm, $[NO_2]_0$ = 0.032 ppm, $[C_3H_6]_0$ = 4.0 ppm v[b]

No.	$[HONO]_0$[c] ppb	$[RCHO]_0$[c] ppb	KOH[d] ppm^{-1}-min^{-1}	$[O_3]_{max}$ ppm	Max. time EST
e	-	-	-	0.61	4:18
1	0.1	1	2.2×10^3	0.32	>5:00
2	0.2	4	2.2×10^3	0.46	>5:00
3	0.1	1	3.2×10^3	0.55	>5:00
4	0.2	4	3.2×10^3	0.61	4:00

[a] Sept 15 diurnal photolytic rate constants assumed and a constant temperature 85°F.

[b] Initial conditions in experiment and simulations

[c] Initial conditions specified in simulations

[d] Rate constant specified for OH + propane

[e] Observed conditions in experiment

in Table 3. Either the high or low choice of initial conditions gave substantial amounts of O_3, and the modeled situation included the conversion of NO to NO_2 before O_3 formation could begin.

Again, one should avoid the conclusion that because it was possible to show agreement between chamber data and a model that either is "correct." It simply means that the RTI observations are not in disagreement with known theory *as expressed* in Dodge's model. Much more extensive testing at other conditions would be required before assuming either was a reasonable representation of actual events.

TABLE 3. COMPUTER SIMULATION RESULTS AT INITIAL CONDITIONS NEAR RURAL CONDITIONS[a]

$[NO_x]_0$ = 0.016 ppm, $[NO_2]_0$ = 0.0032 ppm, $[C_3H_8]_0$ = 0.4 ppm V

No.	$[HONO]_0$ ppb	$[RCHO]_0$ ppb	KOH $ppm^{-1}-min^{-1}$	$[O_3]_{max}$ ppm
1	0.1	1	2.2×10^3	0.152
2	0.2	4	3.2×10^3	0.179
3[b]	0.2	4	3.2×10^3	0.135[b]

[a] LA summer solstice diurnal photolytic rate constants assumed and a constant temperature of 85°F.

[b] Same as 2 but PPN and PAN decomposition reactions (R57, R69 Table 5) omitted.

It is instructive to examine the Dodge model in comparison with the Chang and Weinstock model and in comparison with newer information. Tables 4 and 5 give the reactions and their rate constants used in the inorganic and organic portions of the mechanisms. The reactions have been collected into sequences, and since the inorganic portions were so similar all the reactions were collected together, a notation in the rate constant column indicates when the reaction did not appear in a mechanism.

The principal differences in Table 4 are: Dodge did not use seven of the reactions used by Chang and Weinstock (Reactions 20-25, and 31) because the absolute rates of these reactions at the conditions simulated are very small and their omission was assumed to have an almost undetectable influence. (This may not be true at other conditions.) Likewise, Chang and Weinstock omitted R4.

Dodge used theoretical photolysis rates that varied as a function of zenith angle appropriately for each wavelength range as opposed to a constant ratio to the NO_2 photolysis rate. This wavelength dependence is important for

TABLE 4. COMPARISONS OF INORGANIC PORTIONS OF CHANG AND WEINSTOCK MECHANISM WITH DODGE MECHANISM FOR PROPANE

No	Reaction	Chang Rate Constant	Dodge Rate Constant
1	NO2 → NO + O	k1	k1
2	O + (O2) → O3	2.1E-5[O2][M]	4.4E+6
3	O3 + NO → NO2 + (O2)	25	25
4	O + NO2 → NO + (O2)	not used	1.3E+4
5	O3 + NO2 → NO3 + (O2)	4.8E-3	5E-2
6	NO3 + NO → 2NO2	1.5E+4	1.3E+4
7	NO3 + NO2 → N2O5	4.4E+3	5.6E+3
8	N2O5 → NO3 + NO2	14	24
9	N2O5 → 2HNO3	1.5E-6[H2O]	2E-2
10	O3 → O1D + (O2)	combined	4.9E-3 w/k1=0.52
11	O3 → O + (O2)	3.5E-3 ·k1	2.8E-2 w/k1=0.52
12	O1D → O	4.7E+4[M]	8.7E+10
13	O1D → 2OH	3.1E+5[H2O]	1.0E+10
14	NO + NO2 → 2HONO	1.9E-11[H2O]	2.0E-5 *
15	HONO + HONO → NO + NO2 + (H2O)	1.8E-5	1.0E-3 *
16	HONO → NO + OH	6.8E-2 ·k1	3.0E-2 w/k1=0.52
17	OH + NO → HONO	1.2E+4	1.2E+4
18	OH + NO2 → HNO3	1.5E+4	1.5E+4
19	OH + O3 → HO2 + (O2)	83	87
20	OH + H2O2 → H2O + (O2)	1.2E+3	not used
21	OH + HONO → NO2 + (H2O)	3.1E+3	not used
22	OH + HNO3 → NO3 + (H2O)	1.9E+2	not used
23	OH + CO → HO2 + CO2	210	not used
24	HONO + NO3 → 2NO2 + (H2O)	2.2E-2	not used
25	NO2 + NO2 → HONO + HNO3	8.7E-9[H2O]	not used
26	HO2 + NO → NO2 + OH	700	2000 *
27	HO2 + NO2 → HONO + (O2)	35	not used *
28	HO2 + O3 → OH + (2O2)	22	2.3
29	HO2 + HO2 → H2O2	4.9E+3	4.0E+3
30	H2O2 → 2OH	3.5E-3 k1	1.6E-3 w/k1=0.52
31	HO2 + OH → (H2O) + (O2)	1.5E+5	not used

TABLE 5. COMPARISON OF ORGANIC PORTION OF CHANG AND WEINSTOCK MECHANISM WITH DODGE MECHANISM FOR PROPANE

No.	Dodge Model							Chang and Weinstock Model							
32	O	+	propane	→	IP02	+ OH	22	O	+	propane	→	R02	+ OH	22
33	OH	+	propane	→	IP02	+ (H20)	2400	OH	+	propane	→	R02	+ (H20)	3200
34	OH	+	propane	→	C302	+ (H20)	800							
35	IP02	+	NO	→	N02	+ IPO	2000							
36	IP02	+	H02	→	loss		4000	all peroxyalkyl radicals are treated below						
37			IPO	→	acetone	+ H02	1.5E+6							
38	IPO	+	N02	→	acetone	+ HONO	1.5E+3							
39	IPO	+	N02	→	loss (RN03)		1.5E+4							
40	C302	+	NO	→	N02	+ C30	2000	R02	+	NO	→	N02	+ RO	700
41	C302	+	H02	→	loss		4000	R02	+	H02	→	R00H		4900
42										R00H	$\xrightarrow{h\nu}$	RO	+ OH	3.5E-3·kl
43								OH	+	R00H	→	R02	+ (H20)	1200
44								R02	+	R02	→	RO	+ RO	490
45								R02	+	RC03	$\xrightarrow{O_2}$	R02	+ RO	490
46			C30	$\xrightarrow{O_2}$	C2CHO	+ H02	8.2E+5			RO	→	2/3 RCHO	+ 1/3 HCHO+H02	924
47	C30	+	N02	→	C2CHO	+ HONO	2900	RO	+	N02	→	RN03		110
48										RN03	→	loss		1.0E-4
49	C30	+	N02	→	loss (RN03)		1.5E+4							
50								RO	+	NO	→	RN02		120
51										RN02	$\xrightarrow{h\nu}$	RO	+ NO	3.5E-3·kl

(continued)

TABLE 5. (Continued)

No.	Dodge Model							Chang and Weinstock Model						
52			C2CHO	$h\nu$ →	stable products		2.2E-3							
53			C2CHO	$h\nu$ →	C202	+ H02	2.0E-3	all higher aldehydes are treated as RCHO below						
54	OH	+	C2CHO	→	C3C03		2.1E+4							
55	C3C03	+	NO	→	NO2	+ C202	2500							
56	C3C03	+	NO2	→	PPN		740							
57			PPN	→	C3C03	+ NO2	0.04							
58	C3C03	+	H02	→	loss		4000							
59	C202	+	NO	→	NO2	+ C20	2000							
60	C202	+	H02	→	loss		4000							
61			C20	→	CCHO	+ H02	8.2E+5							
62	C20	+	NO2	→	CCHO	+ HONO	2900							
63	C20	+	NO2	→	loss (RNO3)		1.5E+4							
64			CCHO	$h\nu$ →	stable products		2.3E-5 w/kl=0.52	not used						
65			CCHO	$h\nu$ →	Me02	+ H02	2.6E-3 w/kl=0.52		RCHO	$h\nu$ →	R02	+ H02 + CO	1.2E-3·kl	
66	OH	+	CCHO	→	CC03	+ (H20)	2.1E+4	OH	+ RCHO	→	RC03	+ (H20)	2.1E+4	
67	CC03	+	NO	→	NO2	+ Me02	2500	RC03	+ NO	→	NO2	+ R02	1500	
68	CC03	+	NO2	→	PAN		740	RC03	+ NO2	→	PAN		35	
69			PAN	→	CC03	+ NO2	0.04		PAN	→	R02	+ NO3	0.003	
70	CC03	+	H02	→	loss		4000	RC03	+ H02	→	RC03H	+ 02	4900	
71								RC03	+ RC03	→	R02	+ R02	490	
72								OH	+ RC03H	→	RC03	+ (H20)	1200	
73									RC03H	$h\nu$ →	R02	+ OH	3.5E-3·kl	
74	Me02	+	NO	→	NO2	+ Me0	2000							
75	Me02	+	H02	→	loss		4000							
76			Me0	→	HCHO	+ H02	2.0E+5							

(continued)

TABLE 5. (Continued)

No.	Dodge Model			Chang and Weinstock Model		
77	MeO + NO2 → HCHO + HONO	4400				
78	MeO + NO2 → loss (RNO3)	1.5E+4				
79	HCHO $\xrightarrow{h\nu}$ stable products	5.4E-3 w/k1=0.52		HCHO $\xrightarrow{h\nu}$ CO		1.1E-2·k1
80	HCHO $\xrightarrow{h\nu}$ HO2 + HO2	2.1E-3 w/k1=0.52		HCHO $\xrightarrow{h\nu}$ HO2 + HO2 + CO		4.7E-3·k1
81	OH + HCHO → HO2	2.1E+4		OH + HCHO → HO2 + CO		2.1E+4

aldehyde photolysis for example. The Dodge photolytic rates are quoted for noon.

Dodge used the most recent findings by Chan et al.(10) for HONO equilibrium with NO_2, NO, and H_2O as opposed to the values given by NBS 866. There was, therefore, a factor of 100 in the rates used by the two models.

Dodge used the most recent confirmed rate for R26, which is almost a factor of three higher than the value used by Chang and Weinstock. (See notes after Table 5 for explanations of new rate constants.) This difference is significant.

Dodge did not use R27. (See later discussion concerning the significance of this reaction.)

In short, the Dodge inorganic mechanism should be slightly more reactive than the Chang and Weinstock mechanism.

In Table 5, the organic mechanism portions, substantial differences between the Dodge and Chang and Weinstock mechanism are revealed. These arise partly because a "lumping" scheme was employed by Chang and Weinstock while Dodge used an explicit treatment. All peroxyalky (RO_2) radicals are treated alike by Chang and Weinstock . To account for the decomposition of the RO radicals (R45) formed in the NO oxidation (R39), they introduced a parameter that is supposed to represent the fraction of total aldehydes produced that are not formaldehyde. They gave values of 0, 1/2, 2/3, and 2/4 for methane, ethane, propane, and butane. No justification was given for these values.

In Dodge's model, 75% of the propane consumed formed acetone with no further reaction; 25% of the propane lost was available to be converted into propionaldehyde; formaldehyde arises as a consequence of the degradation of propionaldehyde. Dodge's model also has a greater potential for oxidizing NO to NO_2. Chang and Weinstock's model has more losses for RO_2 and RO and for NO_2. Other comments on rate constants are given in the notes following Table 5.

Dodge commented, "It should be pointed out that the handling of the NO_x chemistry in this system is extremely important. For example, in light of Hendry's recent findings, two reactions were included in this modeling:

$$PPN \rightarrow CH_3CH_2CO_3 + NO_2$$

$$PAN \rightarrow CH_3CO_3 + NO_2$$

A rate constant of 0.04 min^{-1}, which is the rate of PAN decomposition at 85°F, was assigned to these reactions. If these two reactions are eliminated from the model, the O_3 max of 0.179 ppm, obtained in the previous example, drops to a value of only 0.135 ppm. ...Similar effects on O_3 formation can be achieved by varying rate constants for a number of other reactions involving NO_x chemistry."

The Hendry data referred to by Dodge was the finding that PAN chemistry is very similar to N_2O_5 chemistry (37).

$NO_3 + NO \rightarrow 2\ NO_2$	$1.29 \times 10^4\ ppm^{-1}\text{-}min^{-1}$
$NO_3 + NO_2 \rightarrow N_2O_5$	$5.7 \times 10^3\ ppm^{-1}\text{-}min^{-1}$
$N_2O_5 \rightarrow NO_3 + NO_2$	$3.42 \times 10^{16} \exp(-10{,}600/T)\ min^{-1}$

and

$CH_3C(O)O_2 + NO \rightarrow NO_2 + CH_3C(O)O$	$4.9 \times 10^3\ ppm^{-1}\text{-}min^{-1}$
$CH_3C(O)O_2 + NO_2 \rightarrow PAN$	$1.5 \times 10^2\ ppm^{-1}\text{-}min^{-1}$
$PAN \rightarrow CH_3C(O)O_2 + NO_2$	$1.2 \times 10^{18} \exp(-13{,}537/T)\ min^{-1}$

Thus giving the decomposition of PAN a strong temperature dependence.

A more significant possibility, initially suggested by Hendry, is (with rate constants estimated by Jeffries):

$HO_2 + NO \rightarrow NO_2 + OH$	2.1×10^3 ppm^{-1}-min^{-1}
$HO_2 + NO_3 \rightarrow HO_2NO_2$	7.2×10^2 ppm^{-1}-min^{-1}*
$HO_2NO_2 \rightarrow HO_2 + NO_2$	$3 \times 10^{17} \exp(-11{,}685/T)$ min^{-1}*
$HO_2NO_2 \rightarrow HONO + O_2$	0.94 min^{-1}*

*estimated

Although not fully tested by kinetic measurements, this formulation is consistent with data obtained by Niki, Gay, Cox and Derwent, Simonaitis and Heicklen, Calvert and co-workers, and Hendry (38,39,6,40,46,37). It nearly explains the temperature dependence of O_3 formation in the UNC outdoor chamber, and with slight modifications of rate constants (increase in the A factor for HO_2NO_2 decomposition and a decrease in rearrangement rate) it accounts for the temperature dependence of O_3 in the UCR chamber (42). Furthermore, there may be metastable intermediates formed by most RO_2 and NO_2 reactions that would have similar chemistry to that suggested for HO_2 above. Thus, it may be that even the Dodge mechanism, which was quite complete at the time of its formulation, may not adequately represent the actual chemistry occurring in propane/NO_x systems.

The influence of the above reaction sequences on the hot day outdoor model was either accounted for in Dodge's mechanism (N_2O_5 and PAN chemistry), or their influence on the O_3 chemistry would be minimized by the high temperature existing during the run. Recall that Dodge omitted R27, the overall effective reaction for the $HO_2 + NO_2$ sequence, thus assuming total HO_2NO_2 decomposition and no HONO formation by this path. Under cooler temperature conditions, such as those on early mornings, the $HO_2 + NO_2$ sequence could form significant HONO (recall that Dodge used 0.2 ppb initial HONO). If the temperature does not increase, however, this reaction sequence would limit the NO_2-to-NO ratio (and therefore O_3) to values near 10 or 15 to 1.

The Dimitriades and Joshi chamber runs were performed at a reported air temperature of 85°F. This measurement was made, however, by a stainless-steel-encased thermocouple that is permanently installed through one of the

Teflon endplates. It projects 6 to 8 inches into the chamber and is illuminated by the chamber light sources (personal communication from S. Joshi to H. Jeffries, February 1977). Standard meteorological air temperature sensors are always shielded from all radiation sources and aspirated to correctly measure air temperature since the air is relatively transparent to radiant heat.

In the UNC outdoor chamber, a directly exposed temperature sensor inside the chamber showed 10-15°F higher temperatures than the same sensor mounted under the chamber (shielded from the direct sun) and aspirated at high velocities with chamber air. (My digital thermometer when exposed to two 15-watt fluorescent lamps at a distance of 12 inches showed ∿ 6°F temperature rise in one hour.) Thus, it may be reasonable to hypothesize that the reported air temperature in the EPA chamber may be too high by 10-15°F. This hypothesis combined with the HO_2NO_2 chemistry described above may offer partial explanation for the results described below.

Dodge applied her model to the Dimitriades and Joshi propane run that had been modeled by Chang and Weinstock. In this run, $[propane]_o$ = 4.0 ppm], $[NO]_o$ = 0.18 ppm, $[NO_2]_o$ = 0.02 ppm, and ΦKa for NO_2 was 0.33 min^{-1}. Except for the light intensity and the temperature, these were essentially the conditions used in the RTI run. Using the conditions for simulation number 4 in Table 2, Dodge's model predicted only 0.04 ppm O_3 at 450 minutes instead of the 0.11 ppm O_3 at 200 minutes obtained in the actual run. NO_2 had just reached its maximum at 450 minutes in the model, and O_3 was rising. In the chamber, NO_2 maximum occurred at about 70 minutes after irradiation started. Numerous manipulations of model conditions were tried; all were unsuccessful.

If, as hypothesized above, the chamber was actually at 70°-72°F, then the temperature dependence of the peroxyacylnitrate decomposition reactions, the potential temperature dependence of HO_2NO_2 decomposition reactions and, if they occur, other RO_2NO_2 decomposition reactions could have exerted a major effect. Dodge has already demonstrated the importance of PPN and PAN decomposition in this model (see No. 3 in Table 3). Cooler chamber temperatures would lead to higher HO_2NO_2 concentrations and thus greater production of

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HONO, which would serve as an efficient OH source without substantial O_3 production because the NO_2-to-NO ratio would be limited to 10 or 12 to 1. Thus rapid NO to NO_2 could possibly occur without much O_3 formation.

It is therefore recommended that the chamber air temperature at run conditions be verified, and that further modeling studies be performed to determine if the above suppositions have the hypothesized impact in this system.

Thus, there are alternatives to the Chang and Weinstock hypothesis for the Dimitriades and Joshi smog chamber results and, although computer simulation of photochemical mechanisms is a very useful investigative tool of great potential, it does not necessarily represent the "truth." Clearly, a model can be wrong. That a model representation has general validity requires extensive comparisons with actual data obtained under a wide range of conditions. Chang and Weinstock presented no evidence that this was done for their model; therefore disagreements between Dimitriades and Joshi's chamber results and Chang and Weinstock's model have little meaning.

An Approach for Testing for Unreactive Organics

As illustrated by the entries in Table 1, neither smog chamber experimenting nor modeling *used alone* is likely to provide highly reliable answers to the question of whether a particular organic compound is likely to form more than 0.08 ppm O_3 under some reasonable set of atmospheric conditions. Obviously, if this question is to be pursued in a serious and rigorous fashion, *the two methods must be used as a check on each other*. This would require a much larger effort than just performing the smog chamber experiments. Extensive effort should be devoted to understanding the background reactivity problem. Special experiments would have to be designed to provide insight into the processes that are occurring. Bufalini et al. (33) have started a modeling effort for data such as that shown in Figure 1, but their work was data limited. They did not actually try to reproduce the results shown in Figure 1. What is the compound being oxidized? Why does the "NO_x" not disappear?

A large number of experiments must be directed at determining the reproducibility of the smog chamber under various conditions of operation. This may give more insight into the impact of wall-related processes than just clean air irradiations. For example, in Figure 1, the measured NO_x is approaching a value of 16 ppb or a mass of 2.6×10^{-7} moles of NO_x. If the previous run had 0.2 ppm of NO_x (3.28×10^{-6} moles), then 8% of this NO_x had to be retained on the walls after the 38 hours of cleanup treatment. If the clean air run is repeated without an intermediate NO_x/HC run, what are the results? What is the magnitude of the wall source? How long can it keep up? What is the repeatability of a run that, say, just does produce 0.1 ppm O_3? How does this repeatability vary with cleanup procedures, e.g., cleanup with lights on versus cleanup with lights off or no cleanup? In other words, what is the impact of potential wall effects on oxidant production if drastically different cleanup procedures are used (sensitivity analysis).

In addition to dealing with potential wall effects, the smog chamber must be shown to be consistent with general knowledge about reasonable initial concentration HC and NO_x systems. This is where the modeling effort can play its greatest role. Can the system be modeled at a wide range of initial conditions with our current understanding of chemistry? The chamber dependence of the model must be tested by applying it to another chamber. In other words, I would hope that one consistent model could be found that would reasonably predict both an outdoor chamber and an indoor chamber. This would require quality assurance programs for independently calibrated equipment. Initially this modeling effort and data generation for the model would occupy a great deal of time, but once a reasonable agreement had been obtained at a wide range of conditions, only random check runs and remodeling would be required throughout the experimental program. Recognition must be given, however, to the possibility that some unusual organic compounds will be tested that may drastically alter the wall conditions compared to those used in the wall test runs. Therefore, when unusual outcomes are observed, rather detailed tests may be required to ascertain if the chamber has changed its characteristics.

It is my opinion that a combined approach as described above is currently the most reliable method for determining if a given organic compound, when considered by itself with NO_x, is capable of forming O_3 above a given value.

A broader, more philosophical issue, however, is the question of whether the irradiation of single compounds, starting with mostly NO, is an effective test of a compound's ability to participate in atmospheric chemistry and to generate O_3. It may be more realistic, for example, to test the ability of an organic compound, at some upper limit of concentration, to influence the O_3 generation in a hydrocarbon or time limited photochemical system that would normally produce, say, 0.1 ppm of O_3 at a temperature and light intensity reasonably representative of the current high oxidant region of the U.S. The hydrocarbon in the base mixture could be a simple mixture anticipatory of expected urban conditions at some future time or a model auto exhaust/urban emissions mixture. The base system might be, for example, using the O_3 isopleth diagram for the adjusted and unadjusted Bureau of Mines dilute auto exhaust model, an $[NO_x]_o$ of 0.2 ppm and an $[HC]_o$ of 0.5 ppmC. Any compound that, when added to this mixture at levels up to 5 *ppmC*, produced O_3 at the end of a fixed time period exceeding the base systems low mean O_3 value by more than two standard deviations of the base system reproducibility would be declared reactive in the urban environment.

To deal with transport or "rural" reactivity, the base system would be one that had low $[HO_x]_o$ and probably mostly in the form of NO_2, say 0.05 ppm, but ample $[HC]_o$, say 1.0 ppmC, primarily alkane. Such a system, under long irradiation, might produce 0.10 ppm O_3. Again the O_3 resulting from the addition of 5 *ppmC* of the test organic to the base system would be compared with the mean O_3 of the base system plus two standard deviations of the base system's O_3. Any compound that compared high would be declared reactive in the rural environment.

These types of tests are considerably more representative of actual atmospheric situations and address the practical problems of conducting smog chamber experiments in that many of the issues related to so-called wall problems are irrelevant and the inherent precision of the method is built into

the test method. Considerably less chamber testing and modeling would be required with this approach.

RECOMMENDATIONS FOR FURTHER RESEARCH

- Expand upon the work started by Bufalini et al. (33) and develop the information on chamber reproducibility discussed in the preceding section. In particular, experimental evidence related to a possibly enhanced photolysis rate for HNO_3 should be developed. If necessary, the entire 400 liters of the glass/Teflon chamber should be collected by freeze-out at, e.g., 1200 minutes in a run such as that shown in Figure 1, and the trapped materials subjected to gas chromatograph/mass spectrometer analysis.
- Test the proposed HO_2NO_2 mechanism and rate constants as a function of temperature. If supported, determine the most realistic temperature at which to conduct smog chamber experiments.
- Verify glass/Teflon chamber temperature. If it is found to be cooler than thought, remodel chamber results for propane using most recent version of mechanism. If the temperature measurements were correct, repeat propane experiments using different cleanup procedures between runs.
- Investigate methods to determine product yields and stoichiometrics of organic reactions important in photochemical mechanisms.

COMMENTS BY J.G. CALVERT

I have read Jeffries' comments and find few things to fault. Some matters are those of interpretation, which are the best Jefferies (or I) can come up with — who is correct, is a matter one cannot prove.

One final comment refers to p. 20 middle page — he means: "$HO_2 + NO_2 \rightarrow HO_2NO_2$" not "$HO_2 + NO_3 \rightarrow HO_2NO_2$." It seems that we all have a share in the interesting new area of HO_2NO_2. Our work on this is continuing and should shed some light on mechanism alternatives.

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